Appendix D. Site Reports—Japan

OVERVIEW OF NANOPARTICLE / NANOTECHNOLOGY RESEARCH IN JAPAN

Lynn Jelinski

When considered together, the WTEC panel's visits to Japanese sites revealed several important trends that augur well for Japan's success in nanotechnology. These trends include a substantial capital infrastructure, the high quality of the science, vigorous exchange of personnel, existence of mechanisms for scientific renewal, and established and growing collaborations between academia and industry.

Capital Infrastructure. The panel was impressed with the very large and recent investments in capital equipment for nanotechnology and microelectronics, both at the national labs and at universities. In places such as JRCAT, NRIM, ONRI, Osaka University, RIKEN, Tohoku University, and Tokyo University, panelists toured room after room of state-of-the-art fabrication and synthesis equipment, characterization equipment, and carefully designed cleanrooms for micro- and nanotechnology. Given this infusion of capital into infrastructure, Japan is well positioned to assume a leadership role in nanotechnology and nanoparticle science.

Quality of the Science. As would be expected for any large-scale and far-ranging laboratories tour, the WTEC panel encountered some research that mainly takes the work of others and advances it forward, perhaps with a new twist or wrinkle. However, the panel also encountered research groups that are defining the field and creating, rather than riding, the wave of scientific discovery and development. Examples of Japanese institutions where worldwide scientific leadership has occurred or is emerging in nanotechnology and nanoparticles include ETL, the Institute of Molecular Science, JRCAT, Kyoto University, NAIR, NEC, NRIM, RIKEN, and Tohoku University. The organizations that have a world leadership position tend to be those that have chosen a focus area (e.g., organometallic chemistry at IMS; nanoparticle synthesis at Tohoku University), rather than those that have lots of people working on too broad a range of subject areas.

Flow of Personnel and Ideas. The panel was impressed with the large numbers it observed of international postdoctoral fellows, students, visiting scientists, and temporary researchers. There are apparently a number of programs in place in Japan to encourage international collaboration and cooperation. This flow of scientists and ideas in the field of nanoparticles and nanotechnology suggests that international scientists feel they have much to learn from Japan. This open flow of personnel also ensures that Japan has ready and early access to new ideas and technologies from abroad.

Mechanisms for Scientific Renewal. Focusing on the national labs such as IMS, NAIR, NRIM, and RIKEN, the team was impressed with their agility in moving into new scientific areas. Panelists heard of mechanisms to close down nonproductive programs, mechanisms to ensure fresh turnover of faculty (e.g., at IMS), and mechanisms to develop consensus on new areas of science (e.g., the Intelligent Materials Forum). Such mechanisms will help ensure Japan's leadership role, not only in nanotechnology and nanoparticle science, but in many other important areas of research and development.

Collaborations Between Academia and Industry. The panel was impressed with the large number of collaborations evident between academic labs and industrial workers. Many of the academic labs are staffed with long term visitors from industry. A single lab may have workers from competing industries, working side-by-side on company-specific projects. There does not appear to be particular concern about intellectual property rights.

Site: **Electrotechnical Laboratory (ETL)**
Ministry of International Trade and Industry (MITI)
1-1-4 Umezono, Tsukuba-shi
Ibaraki 305, Japan
Tel: (81) 298-54 5220; Fax:(81) 298-54 5088,

Date Visited: 22 July 1997

WTEC: R.W. Siegel (report author), D.M. Cox, H. Goronkin, J. Mendel, H. Morishita, M.C. Roco

Hosts: Dr. Koichiro Tamura, Director-General of ETL
Dr. Tsunenori Sakamoto, Director of Electron Devices Division; E-mail: tsakamot@etl.go.jp
Dr. Masanori Komuro, Leader, Micro-Beam Section, Electron Devices Division
Dr. Junji Itoh, Electron Devices Division
Dr. Hiroshi Yokoyama, Leader, Molecular Physics Section, Supermolecular Science Division
Dr. Hiroyuki Oyanagi, Leader, Exotic Matter Physics Section, Physical Science Division

BACKGROUND

The afternoon of July 22 from 13:30 to 16:00 was spent at the Electrotechnical Laboratory (ETL) of the Agency of Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry (MITI). It is more than 100 years old and is the largest national laboratory in Japan, with ~ 530 researchers and an annual budget of $100 million, according to a general introduction to ETL presented by its Director-General, Dr. Koichiro Tamura. Of this budget, ~ 15-20% is currently focused on various aspects of nanotechnology. The four major fields of research and development activities at ETL are (1) Electronics and Bioelectronics, (2) Energy Technology, (3) Information Technology, and (4) Standards and Measurement Technology.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

The work in the Electronics and Bioelectronics area, in which most of the nanotechnology efforts reside, is carried out primarily in four divisions, which are themselves each comprised of several sections. These divisions, their constituent sections, and their respective leaders are as follows:

Physical Science Division (Dr. Hajime Shimizu)

Fundamental Physics Section (Dr. Shuji Abe)
Exotic Matter Physics Section (Dr. Hiroyuki Oyanagi)
Electron Physics Section (Dr. Hajime Shimizu)
Applied Physics Section (Dr. Shin-ichi Kuroda)

Materials Science Division (Dr. Kazuo Arai)

Materials Fundamentals Section (Dr. Hideyo Okushi)
Nonequilibrium Materials Section (Dr. Akihisa Matsuda)
Quantum Materials Section (Dr. Sadahumi Yoshida)
Superconducting Materials Section (Dr. Hideo Ihara)
Optoelectronic Materials Section (Dr. Toshiro Tani)

Electron Devices Division (Dr. Tsunenori Sakamoto)

Device Functions Section (Dr. Shigeki Sakai)
Device Synthesis Section (Dr. Toshihiro Sekigawa)
Process Fundamentals Section (Dr. Keizo Shimizu)
Micro-Beam Section (Dr. Masanori Komuro)
Microstructure Electronics Section (Dr. Kazuhiko Matsumoto)
Superconductivity Electronics Section (Dr. Akira Toukairin)

Supermolecular Science Division (Dr. Tetsuo Moriya)

Molecular Physics Section (Dr. Hiroshi Yokoyama)
Molecular Electronics Section (Dr. Hideaki Shimizu)
Molecular and Cellular Neuroscience Section (Dr. Toshio Iijima)

After an introduction to the ETL, our host, Dr. Tsunenori Sakamoto, Director of the Electron Devices Division, kindly provided answers to the questions posed by the WTEC panel prior to its visit. He said that his researchers are focusing on a single-electron device that can operate at room temperature ("smaller is better") using scanning tunneling microscopy (STM) and electron-beam fabrication technologies, but he indicated that they were not yet successful. ETL is seven years into its 10-year Quantum Functional Device (QFD) Project (1990-2000), having spent about $40 million so far, with $8-9 million per annum anticipated for the remainder of the project. According to Dr. Sakamoto, the proposals for the direction of ETL's work come "randomly" from industry, university, laboratory researchers, and MITI officials. His division expects a follow-on project on one-electron devices, and he also indicated that MITI has begun a new five-year project on fullerenes/nanotubes in Tsukuba at the National Materials Laboratory with funding of $20-30 million for five years. Collaborations between ETL and the U.S. National Institute of Standards and Technology exist in the areas of STM and liquid crystals.

Technical presentations and laboratory visits followed. The laboratory facilities at ETL are extensive and excellent. They are typical of a mature and well funded research establishment in that all the necessary equipment is available, but the excesses have been avoided of other newer laboratories the panel visited, where there sometimes seemed to be more new expensive equipment than people to use it effectively.

Dr. Sakamoto continued with a description of some research activities at ETL on nanotechnology. He described an STM nanooxidation process for creating a one-electron device showing quantum blockade behavior. The process consists of an STM tip with a water droplet between it and a 3 nm thick layer of Ti on an SiO_2 layer on an Si substrate. TiO_x is formed at the STM tip/H_2O/Ti interface. ETL researchers are also doing this on stepped alpha-Al_2O_3 substrates. This technology has now flowed into other laboratories.

Dr. Masanori Komuro then described an electron-beam writer with a 3 nm diameter beam in ultrahigh vacuum—UHV (10^{-9} torr). Since the normal resolution of polymer resists (e.g., PMMA) with electron-beam lithography and a 50 keV electron gun is about 10-20 nm, higher resolution is needed. His staff report being able to do much better, yielding smaller features, with SiO_2 films using electron beam lithography. A single-electron transistor, written by W dots or wires from WF_6 using electron-assisted deposition, was reported to operate at 230 K.

Dr. Junji Itoh, standing in for Dr. Seigo Kanemaru (Senior Researcher in the Electron Devices Division), then reported on nanostructure activities in the area of vacuum microelectronics. Work was being carried out to create ultraminiature field-emitter tips (Mo, Si) for field emission displays. The tips have about 10 nm radii, can be created in two-dimensional arrays, and show increased emission levels. Because of problems with the stability of emission currents in conventional tips from reduced gas adsorption from the ambient atmosphere, development of MOSFET-structured emitter tips is being pursued, which will enable the combination of light emission and Si-based electronics on the same device structures.

Next, Dr. Hiroshi Yokoyama, Leader of the Molecular Physics Section, described ETL's Scanning Maxwell-stress Microscope (SMM), a new instrument that can look at nanoscale electrical characteristics (work function or charge distribution) as well as structure (topography) by detecting electric long range forces with about 1 mV sensitivity. The instrument is based on an STM or atomic force microscope (AFM), but by oscillating the probe (tip), it is possible to obtain additional information regarding dielectric constant, etc. (Yokoyama et al. 1994; Yokoyama and Inoue 1994). With the SMM, it is even possible to look at living cells under water. The instrument is in use at ETL in various experimental forms, but it is also now beginning to be commercialized by Seiko Instruments (in a price range of $500 thousand to $1 million) in a UHV version with variable temperature capabilities (70-500 K) and both SMM and AFM modes of operation. Future directions for the research work in this area will investigate semiconductor nanodevices under UHV conditions and problems in nanobiology under water. New functionalities for the SMM will be developed using higher frequencies to investigate band structure and the effects of doping, as well as optoelectrical investigations in combination with near-field optical microscopy (an effort funded by AST).

Finally, Dr. Hiroyuki Oyanagi described some work in the Physical Science Division on probing nanostructures with EXAFS. Dr. Oyanagi's group has a close relationship with a number of other groups worldwide. Its EXAFS studies are being carried out at an undulator beamline at the Photon Factory about ten miles from Tsukuba. They have been able to induce local melting by optical excitation and subsequent quenching-in of disordered regions in Se, and they are hoping to use this method for memory applications, if it can be done microscopically. Dr. Oyanagi also mentioned very briefly some work going on in ETL's Materials Science Division on nanostructured one-dimensionally modulated GaAs quantum well systems.

REFERENCES

Yokoyama, H., T. Inoue, and J. Itoh. 1994. *Appl. Phys. Lett*. 65:3143
Yokoyama, H., and T. Inoue. 1994. *Thin Solid Films* 242:33.

Site: **Hitachi Central Research Laboratory**
Planning Office
1-280 Higashi-Koigakubo
Kokubunji-shi
Tokyo 185-8601, Japan
Fax: 81-423-27-7695

Date Visited: 22 July 1997

WTEC: E. Hu (report author), L. Jelinski, C. Koch, D. Shaw, C. Uyehara

Hosts: Dr. Shigeo Nagashima, Deputy General Manager and Head of the Planning Office
Dr. Tadashi Ikeda, Head, Research Cooperation Center, Planning Office
Ms. Yuko Nakamura, Research Cooperation Center, Planning Office
Dr. Masanobu Miyao, Head, Electronics Material Center, Electron Devices Research Department
Dr. Toshio Katsuyama, Sr. Researcher, Optoelectronics Research Department
Dr. Atsushi Kikukawa, Research Scientist, Advanced Research Laboratory
Dr. Masaaki Futamoto, Chief Research Scientist, Information Storage Research Department.
Dr. Kazuo Yano, Sr. Researcher, Systems LSI Research Department

INTRODUCTION

The Research Cooperation Center Planning Office of Hitachi Central Research Laboratory hosted the WTEC team's visit. We were greeted by Dr. Shigeo Nagashima, Deputy General Manager and Head of the Planning Office. Exact figures were not available as to the representation of nanotechnology research at Hitachi.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Dr. M. Miyao discussed the enhanced emission of light from SiGe quantum well devices, relating the quality of light emission with the quality of the interfaces of the quantum well, and the correlation lengths between Ge atoms.

Dr. T. Katsuyama gave a presentation on exciton-polariton quantum wave devices, achieved through confinement of excitons within quantum wires. He discussed a number of novel ways of forming the quantum wires. One method involved the formation of Au islands on GaAs or InAs surfaces. Upon heating, these Au dots formed liquid alloys of In/Au or Ga/Au. For substrates immersed in an arsine/trimethylgallium ambient, the liquid droplets provided the nucleation points for the selective growth of compound semiconductor whiskers (or quantum wires) as long as 1.5 µm, with a 15 nm diameter.

Dr. A. Kikukawa discussed some ways of achieving ultrahigh density recording using indentation by an atomic force microscope (AFM) tip (Fig. D.1). In addition to the recording of data through AFM indentation, read-out by AFM was also characterized. Dr. Kikukawa claimed a read-out rate of 1.25 MB/s with a 25 nm pit size.

Dr. M. Futamoto gave an excellent presentation on ‘near-term’ issues for improved materials for magnetic storage. He showed some examples of materials control at the nanostructure scale required for the formation of magnetic materials suitable for magnetic recording and novel magnetic “spin valves” (Fig. D.2). He showed charts on trends in recording areal density (Fig. D.3) and perpendicular recording using CoCrTa (Fig. D.4).

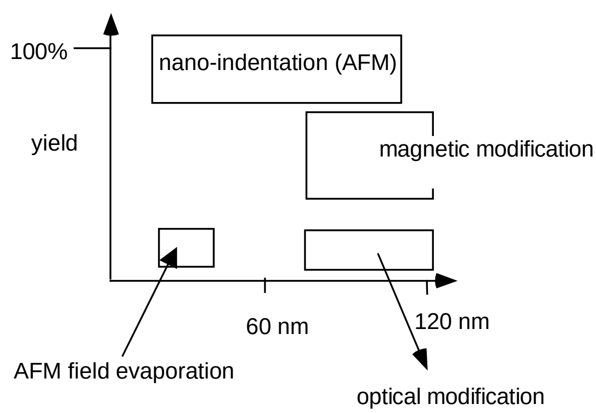


Figure D.1. Concept for high density data recording using nano-indentation (Hitachi).

50Å Ta
300Å CrMnPt
30Å Co
25Å Cu
10Å Co
50Å NiFe
50Å Ta

Figure D.2. Spin valve structure.

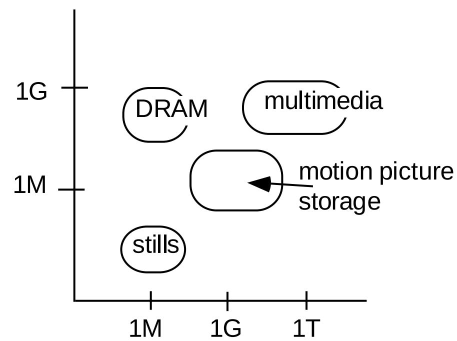


Figure D.3. Need for storage capacity, in bytes (Hitachi).

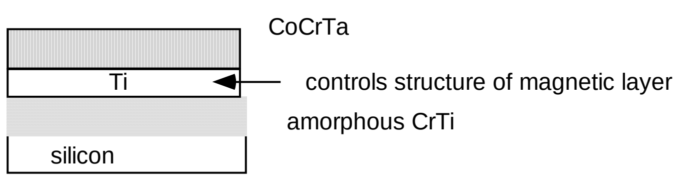


Figure D.4. Perpendicular recording using CoCrTa (Hitachi).

Dr. K. Yano discussed single-electron transistor (SET) memory schemes (Fig. D.5) where quantum dots would form the gate of the device. He described a memory cell (0.8 µm x 0.5 µm) comprising the SETs, using a 2.5 V signal to carry out the 'reading' of the information bit, 10 V to erase a bit, and 15 V to write a bit. Although 10^7 write and erase cycles have been demonstrated, the operation of this memory cell is still rather slow (on the order of microseconds). Dr. Yano suggested that SET technology might be more easily demonstrated in memory devices, rather than in logic devices.

Dr. Yano also described work on novel polysilicon transistors (Fig. D.6) and on ladder-shaped memory cell arrays based on single-electron transistors (Fig. D.7).

The WTEC team's hosts were pessimistic about single-electron logic, stating that reliability requirements are severe. They stated that memory is different—it is possible to use conventional CMOS circuitry to insert different cell structures.

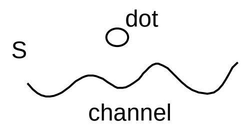


Figure D.5. Single electron memory concept.

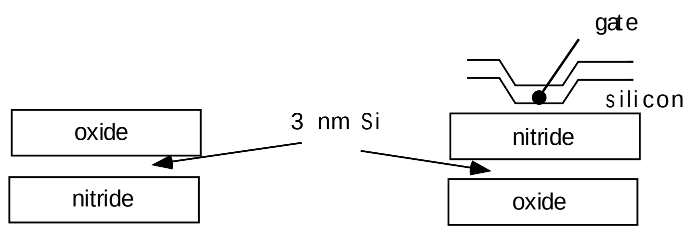
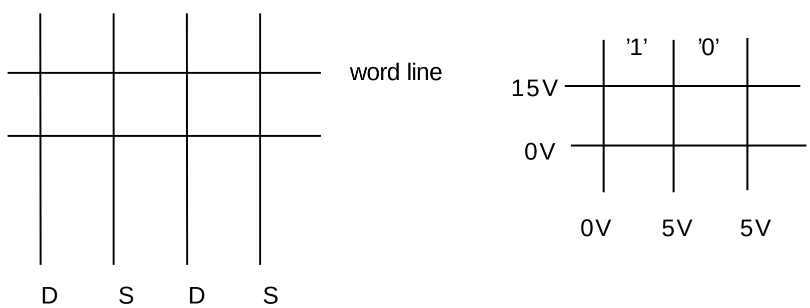


Figure D.6. Polysilicon transistors.



read 2.5 V, erase -10 V, write, 15 V
0=0.01 nA, 10 seconds, slow writing time at 9 V
w/erase 10 µsec, still slower than DRAM
showed 10^7 write/erase cycles

Figure D.7. Ladder-shaped memory cell array.

Site: **Institute for Molecular Science (IMS)**
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Date Visited: 23 July 1997

WTEC: L. Jelinski (report author)

Hosts: Dr. Mitsuo Ito, Director-General
Dr. Mitsuhiko Shionoya, Professor
Dr. Makoto Fujita, Associate Professor
Dr. Takahiro Kusukawa, Assistant Professor
Dr. Tatsuhisa Kato, Associate Professor
Dr. Kyuya Yakushi, Professor
Dr. Yoshihito Watanabe, Professor

BACKGROUND

The Institute for Molecular Science (IMS) is one of three institutes under the umbrella of the Okazaki National Research Institutes. The other two are the National Institute for Basic Biology and the National Institute for Physiological Sciences. Together, they employ over two hundred professionals and about 180 technical and support staff. Each of the three Institutes is headed by a Director-General, who reports to the President. The Institutes are funded by the Ministry of Education, Science, Sports, and Culture (Monbusho).

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Research at IMS is directed toward understanding the properties of molecules and molecular assemblies, and to the design and synthesis of new materials, especially those with novel properties. IMS is strongly oriented toward basic research. The faculty members have few teaching duties and can devote themselves full-time to research.

IMS has an unusual, almost Harvard-like method for ensuring that research remains fresh and of high quality: it imposes the rule that none of the assistant and associate professors can remain at IMS as full professors. Instead, they must go to another institution for promotion, as IMS always hires its full professors from outside. The faculty members with whom I spoke, including junior professors, thought that this policy worked quite well.

Research at IMS that falls within the scope of this report is in the general category of synthesis of novel materials, some with inspiration from biology and some with biomolecules as the building blocks. Most of the work that involves nanoparticles involves some form of organometallic chemistry. The hallmarks of the research are two-fold: creativity, and the soundness by which the new materials are characterized and evaluated. Much of the research the WTEC team saw on this visit has been published in high quality journals such as *Nature* and the *Journal of the American Chemical Society*, attesting to the international reputation of IMS and the high quality of the research. Several of the faculty members have good collaborations with other scientists in Japan. One has an ongoing and productive NSF-funded collaboration with the University of Rochester, and another introduced the visiting WTEC team member to a visiting researcher, on leave from Emory University, who was spending six months in his lab.

Japan seems to be in a leadership role in the production of metallofullerenes. IMS has a large-scale facility for producing fullerenes, and Prof. Kato has been successful in producing C_{82} that contains Sc, Y, and La *inside* the cage structure. Kato is now using the metal inside the fullerene as a way to "tune" the reactivity of the outside. For example, he has shown how LaC_{82} can be reacted with disilanes and diazo compounds to form adducts. A combination of electron spin resonance (ESR) and theory is being used to explain the reactivity of the precursor and the products obtained. One could imagine how this ground-up assembly of nanomaterials could be polymerized to produce larger molecules with novel properties.

Another area of research involves the characterization of magnetic transport and optical properties in phthallocyanines (Pc). Of special interest is $PtPc(AsF_6)_{0.5}$, whose transport properties are being studied under high pressure.

Prof. Shionoya, a very young full Professor who recently came to IMS from Hiroshima University, is using novel combinations of DNA, metal ligands, DNA templating, and proteins to produce molecular wires and molecular hoops through which DNA could be threaded. He is also using double-stranded peptides whose helix pitch could be controlled by an entrained copper that could be induced to go from $Cu(I)_{tetrahedral}$ to $Cu(II)_{square\ planar}$, perhaps by electrons delivered by an STM tip. Figure 7.6 (p. 123) summarizes Prof. Shionoya's vision of how bioinspiration could be used to produce nanodevices.

In a very creative and careful series of single point mutations, Prof. Watanabe has uncovered evidence for, and verified the existence of a "push-pull" mechanism for cytochrome *C* peroxidase. This was done by drawing an analogy between peroxidase and cytochrome P-450, and using insights gleaned from similarities in the active site.

Finally, Prof. Fujita's work involves the approach of using self-assembly by transition metals to form organized large structures. He has been able to make various nanocages, which have potential applications for controlled drug release. He has also used three-dimensional organometallic cage compounds to achieve a "ship-in-a-bottle" synthesis of organic molecules and is currently producing nanostructured molecules with larger cavities than have ever been made before.

Site: **Joint Research Center for Atom Technology (JRCAT)**
Angstrom Technology Partnership (ATP)
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1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan
Tel: (81) 298-54 2570; Fax: (81) 298-54 2575

Date Visited: 22 July 1997

WTEC: R.W. Siegel (report author), D.M. Cox, H. Goronkin, J. Mendel, H. Morishita, M.C. Roco

Host: Dr. Eiichi Maruyama, Executive Director and General Director of Research Center
E-mail: maruyama@jrcat.or.jp

BACKGROUND

Tuesday morning 9:30 to 12:00 noon of 22 July was spent in Tsukuba visiting the Joint Research Center for Atom Technology (JRCAT), an organization founded in February of 1993 through a joint contract between the National Institute for Advanced Interdisciplinary Research (NAIR) and the Angstrom Technology Partnership (ATP). These latter organizations were created by the Agency of Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry (MITI). The central focus of JRCAT is the Atom Technology Project, a ten-year effort begun by AIST in fiscal year 1992 as one of its Industrial Science and Technology Frontier Programs under the official title, *Research and Development of Ultimate Manipulation of Atoms and Molecules.* AIST's total ten-year budget for this project is about ¥25 billion (~ $250 million), which flows mostly (~ 90%) through the New Energy and Industrial Technology Development Organization (NEDO) and hence ATP, with the balance (~ 10%) flowing directly through NAIR. The distinct advantage of this imbalance for JRCAT is that the NAIR funds are hard (national) monies that cannot be used for hiring people, while the ATP funds are soft (invested) monies that can be used very flexibly. The Atom Technology Project is envisioned as comprised of overlapping efforts in atom manipulation, nanoscale self-organization, and critical-state phase control based on in situ dynamic measurement and control complemented by *ab initio* calculation.

The WTEC panel visit was hosted by Dr. Eiichi Maruyama, Executive Director of ATP and the Atom Technology Project Leader, who presented a very informative and extensive introduction to JRCAT and its research efforts. JRCAT presently has 36 administrators and about 100 research scientists, of whom 35 are from industry, 28 are from national laboratories, 7 are from universities, 26 are postdocs, and four are PhD candidates. About 60% of the scientific staff are supported from ATP and 40% from NAIR. Of these, there are 78 PhDs, 21 foreign scientists, and 3 female scientists. The total funding flow has been reasonably steady since FY1995 at about ¥2.5 billion per annum, with significant fluctuations in the first three years for initial capital expenditures. The publication of research results in "major" journals (i.e., those with high citation impact factors, such as *Nature*, *Science*, *Physical Review Letters*, *Applied Physics Letters*, and *Physical Review B*) appears to be used as a measure of research program success. There have been a significant number of such publications (~ 120 per year) from JRCAT during FY94-FY96.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

The Atom Technology Project research program is lead by Project Leader E. Maruyama along with Deputy Project Leaders K. Tanaka (experiment) and K. Terakura (theory) and is organized into 11 groups in four general areas. These are as follows (with leader):

Solid Surface and Solid Material

- Measurement and control of atomic level structures by mechanical probe—19 scientists (H. Tokumoto)
- Observation and formation of atomic scale structure using beam technology—8 scientists (M. Ichikawa)
- Measurement and control of surface reactions for nanostructure fabrication—7 scientists (M. Ozeki)
- Atomic level analysis and control of II-VI semiconductor surface—6 scientists (T. Yao)
- Exploration of transition metal oxides and organic molecular system—8 scientists (Y. Tokura)
- Exploration of amorphous semiconductors, magnetic thin films, solid-liquid interfaces—15 scientists (K. Tanaka)

Cluster in Free Space

- Formation and control of clusters in ion trap and on solid surface—4 scientists (T. Kanayama)

Organic Molecular Structure

- Scanning probe microscopy (SPM) and optical analysis for DNA and organic molecular structure—11 scientists (T. Okada)

Quantum Simulation of Atomic and Molecular Processes

18 scientists are working on several programs, including the following:

- Organic molecular system, new techniques for computer simulation (K. Terakura)
- Semiconductor materials (T. Uda)

The theory group is also responsible for the JRCAT Supercomputer Laboratory, introduced in March 1994.

Formal evaluation of the research program is held only at its midpoint (six years) and end (ten years), but annual reports are produced. Successful efforts are expected to be transferred to industry. Some projects are continued under new programs, and others are terminated after these evaluations. The second phase (next 4 years) of JRCAT will see increased collaboration with industry, a new study on spin-electronics applications, and an effort to maintain top-level atom technology. The primary scope of the Atom Technology Project will continue to include nanostructure formation and control of surfaces and interfaces (especially in semiconductor and related materials); spin electronics (new materials and measurements); observation and manipulation of atoms and clusters; and theoretical simulation (emphasizing good interaction with experimental groups).

In carrying out its mission, JRCAT interacts with foreign universities via contact and exchange of scientists (e.g., with the University of Birmingham in the UK). Also, the science and technology laws in Japan were changed ca. 1995 to allow Japanese university professors to have more significant interaction with JRCAT and other industries.

The WTEC panel also made visits to four JRCAT research laboratories, the Advanced Interdisciplinary Laboratories of Drs. K. Tanaka, K. Ichikawa (H. Watanabe, host) and Y. Tokura (A. Asamitsu, host), and the Theoretical Research Laboratory of Dr. K. Terakura. The group of Dr. H. Tokumoto was unfortunately away at a conference that day; it is active in attempts to create nanoscale ferroelectric domains by scanning force microscopy (SFM) for nonvolatile, high density memories, sensors and actuators, but is mainly working at the micron scale at present. It also works on self-assembled monolayers (SAM) on surfaces, particularly those that are electrically conductive. All of the groups are extremely well equipped with all of the latest facilities and capabilities necessary to carry out their respective missions.

The Tanaka group laboratory is located in a specially vibration-isolated separate building in the NAIR facilities. The primary research themes of this group are (1) fabrication of semiconductor nanostructures and investigation of their defect structure, (2) creation of magnetic superstructures and searching for new magnetic materials, and (3) elucidation at atomic/molecular levels of the electric double layer at solid-liquid interfaces. Work is ongoing in developing high resolution Raman spectroscopy for the study of molecules on surfaces. It was reported that information from individual molecules can be obtained by coupling to surface plasmon polarization, which enhances the signal by three orders of magnitude. Also, atom manipulation (atom and layer removal) by scanning tunneling microscope (STM) tips is being carried out on Si (mainly) and high temperature superconductors in a UHV-STM without damaging the surrounding regions.

The Ichikawa group has as its primary research themes (1) development of an atomic manipulation system using beam technology and extremely high vacuum pumping, (2) development of surface/interface characterization technologies, and (3) exploration of surface/interface reactions useful for nanostructure formation. The laboratory contained a state-of-the-art 30 keV UHV field-emission scanning electron microscope (SEM) with an SPM being used for Si-based nanostructures. For this development project, a unique STM with atomic resolution was developed on a 6-axis manipulator in the UHV-FE-SEM, but because of unique problems with vibration isolation, the system requires a special isolation room. Electron holography using a biprism to produce 2 coherent beams from the FE (field emission) gun was also in place on the SEM and was being used to create nanoperiodic structures (with 17 nm wavelengths) on SiO_2. In another major development project, a multifunctional Surface Analysis System, with Auger analysis with a 1.4 nm diameter beam probe, was built in this group. About $2.5 million was spent on each of these two major development projects.

The Tokura group (also partly at the University of Tokyo) focuses on the synthesis and physics of oxide electronic materials and organic molecular systems. Examples of current work are the floating-zone crystal growth, in a parabolic mirror image furnace (manufactured by NEC), of large single crystals (e.g., $Pr_{0.65}Cu_{0.35}MnO_3$); investigation of natural one-dimensionally modulated nanostructured superlattices (….+ insulating + magnetic + insulating +....) for giant or colossal magnetoresistance (GMR or CMR) applications; and studies of electric-field-induced resistivity changes in …. + insulating + metallic + insulating + metallic + ... multilayers, such as $Pr_{1-x}Ca_xMnO_3$ (e.g., $x = 0.3$), below 100 K. A main focus of the group’s research is using laser ablation to build layers by cluster assembly on stepped substrates of $SrTiO_3$ for functional device applications. A system with five movable targets and a fixed laser is being used for this work, and the studies are carried out as a function of substrate temperature and oxygen partial pressure.

Finally, the WTEC team visited the Terakura theory group, led by Dr. Kiyoyuki Terakura, who has been at JRCAT for about three and a half years. This world-class theory group specializes in first-principles, state-of-the-art quantum simulations of atomic and molecular processes in the areas of semiconductor surfaces, transition metal compounds, and exotic materials such as conducting organic solids (e.g., DCNQI-M, with M = Li, Ag, Cu). The group also develops new computational methodologies for approaching such problems and is responsible for the large-scale supercomputer system at JRCAT, consisting of two main computers—a vector-parallel computer (VPP500/32) and a massively parallel computer (128 node CM-5E). The theory group has good interactions with the experimental efforts at JRCAT; although frequently the experimentally investigated systems can be rather complex for fundamental theoretical simulation, serious theoretical efforts are made to benefit the experimental program. The Terakura group also has extensive external collaborations with NEC, Hitachi, Fujitsu, and various universities in Japan and abroad. In addition to its normal publications, the theory group disseminates the results of its efforts in a series of well-prepared annual reports.

Site: **Kyoto University**
Graduate School of Energy Science
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Kyoto 606-01, Japan
Fax: (81) 75-753 5464

Date Visited: 25 July 1997

WTEC: C. Koch (report author), D.M. Cox, J. Mendel, H. Morishita, R.W. Siegel

Host: Professor Paul Hideo Shingu, Dean

BACKGROUND

This visit concentrated on the laboratory of one professor, Professor Paul Hideo Shingu at Kyoto University. He has a group of associates and graduate students (about 15) and is funded by the Ministry of Education, Science, Sports, and Culture (Monbusho).

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Professor Paul Hideo Shingu was the WTEC panel's host. He is the Dean of the Graduate School of Energy Science at Kyoto University. He is a pioneer in the use of severe mechanical deformation to produce nanocrystalline (nc) microstructures. He was the first researcher to demonstrate the synthesis of nc materials by mechanical alloying (high energy ball milling) in the Ag-Fe immiscible system in a paper published in 1988. His group was the first to point out that nc materials can be made by MA. Much of his group's work in this area is summarized in a paper by P.H. Shiugu in *Materials Transactions JIM* 36:96 (1995). In order to be better able to define the mechanism(s) involved in creation of nc materials by severe plastic deformation, Prof. Shungu turned to the method of repeated press-rolling of component foils or powder mixtures. This "deterministic" mechanical alloying has allowed for both experimental studies of the developing microstructure—by, for example, high resolution transmission electron microscopy (HRTEM)—and the modeling of the microstructure by computer simulations. He and his coworker, Dr. K.N. Ishihara, have used chaos theory to model the microstructure obtained in shearing of dissimilar components, based on several simple approaches such as the baker's transformation, linear shear, and parabolic shear. The iteration of certain mapping generates chaos. It is noted that the application of precisely deterministic mapping can generate a chaotic mixing of initially macroscopically separated structures by a surprisingly small number of repeated applications of a mapping. This is analogous to the structures observed experimentally due to the mechanical deformation.

Among the systems Shingu's group has studied are immiscible systems such as Ag-Cu and Cu-Fe, which form metastable solid solutions; Ag-Fe, which forms an nc composite microstructure; and Co-Cu, which exhibits the giant magnetoresistance (GMR) effect.

The preparation of multilayers by repeated rolling requires careful control of the process. Component foils (or powder compacts) are first annealed in vacuum, pressed together in vacuum, annealed, then repeatedly rolled and annealed. The selected annealing temperature is critical to maintaining the planarity of the layers and to avoid their spheroidization, while relieving the deformation strains to allow further rolling.

HRTEM of the layered structures reveals nc grains within the layers, with rotation of the grain into an apparent epitaxial relationship with the other component.

The panel's other observations on this visit include the following:

- the rolling of mixed powder compacts has produced results similar to those with foils
- a number of mechanical and magnetic measurements have been made on these samples
- it is believed this method of repeated rolling could be scaled up to commercial quantities, since rolling technology is well developed in the steel industry, as one example
- Shingu's group consists of several professionals, one technician, and 15-20 graduate students

A tour of the laboratory facilities revealed several critical processing devices such as a pseudo hot isostatic press (HIP), a good four-high rolling mill, and a vacuum hot press. Characterization facilities, such as a transmission electron microscope, are shared with others in the Department.

Professor Shingu's research differs in the smaller scale of his effort from that carried on by the large groups at national laboratories and IMR at Tohoku University. However, the innovative and creative studies done in his group have made significant contributions to the field of nanostructured materials.

REFERENCE

See also Yasuna et al. 1997. *J. Appl. Phys.* 82(5):2435-2438.

Site: **Nagoya University**
Department of Crystalline Materials Science
Furocho, Chikusa-ku
Nagoya 464-01, Japan
Fax: (81)-52-789-3821

Date Visited: 25 July 1997

WTEC: D. Shaw (report author), E. Hu, L. Jelinski, M.C. Roco, C. Uyehara

Hosts: Professor Uichiro Mizutani
Professor Toshiharu Fukunaga
Professor Nobuo Tanaka
Professor Jun-ichiro Inoue

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Professor Toshiharu Fukunaga, Nanoparticles by Mechanical Milling

The X-ray diffraction spectrum of milled graphite was the same as for amorphous material. The density decreased from 2.2 to 1.85 g/cm^3 in 36 hours of milling. Neutron diffraction confirmed the disorder. These results were analyzed to calculate the radial distribution factor that gives the coordination number, which reduced from 3.01 to 2.82 in the 36 hours. It is believed that this describes production of dangling bonds in the milled material. Assuming the crystalline structure is unchanged upon milling, only the size of the particles changes and the coordination number decreases. The size was estimated to be about 27 Å.

Transmission electron microscopy (TEM) before milling showed a layered graphite-like structure. After milling the material was amorphous.

Ball milling is done at low temperature. The equipment has a 150 G (x gravity) capability but 10 G is used in work in this department.

Trigonal selenium was also milled. Using the same analytical procedures as above, it was estimated that the particles contained about 22 atoms.

Li and graphite were milled together. The Li incorporates into the graphite and coats the balls to produce a gold-colored LiC_6 film. The Li is inserted into the hexagonal C network if the milling intensity is kept low. The potential application is to batteries. One of the technical challenges is to remove the material from the balls.

Professor Nobuo Tanaka, Electron Microscopy

Prof. Tanaka described nanobeam drilling using e-beam, which showed approximately 1 nm square windows drilled with a cylindrical beam. The lattice was distorted around the periphery of the window.

Tanaka discussed a number of other issues, including granular magnetoresistive structures and mass production of fine particles, but it was not clear whether the work was done at Nagoya University or pulled from the literature.

Tanaka showed a video of two sharp gold tips coming together to create a liquid-like interface. The tips were electrolytically sharpened. As seen in the video, the tip diameter was about 10-15 atoms. As the tips separated, the liquid-like region took on the lattice constant of one of the two tips. Previously, this demonstration had been reported with a tip and a flat surface.

Professor Jun-Ichiro Inoue, Transport Phenomena in Macroscopic Magnets

Prof. Inoue has calculated the magnetoresistance ratio vs. surface/volume ratio of FeCr granules in a matrix. The model was independent of matrix material and distance between clusters. Although the assumed spacing was 2-5 Å, interactions were not included. Data from Tohoku University of a tunnel diode with Co-AlO granular barrier had a four order of magnitude drop in resistivity and a constant MR ratio of about 19% at 4.2 K. The barrier thickness was about 1.0 µm, and the maximum voltage was 1.0 V. Typical barrier thickness reported in the literature is about 10-15 Å, so the Tohoku data applies to fields that are about 1E7 lower than structures designed for memory cells or hard drive heads.

The decrease in resistivity was explained by the charging energy of the single-electron-like granules, although this explanation seems unlikely to this author.

Site: **National Institute for Advanced Interdisciplinary Research (NAIR)**
Cluster Science Group
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Tsukuba, Ibaraki 305, Japan
Tel: (81) 298-54 2540; Fax: (81) 298-54 2949

Date Visited: 23 July 1997

WTEC: D.M. Cox (report author), H. Goronkin, E. Hu, J. Mendel, H. Morishita

Host: Dr. Harutoshi Takeo, Leader of Cluster Science Group
E-mail: takeo@nair.go.jp

BACKGROUND

NAIR, the National Institute for Advanced Interdisciplinary Research is one of 15 research institutions of AIST, the Agency of Industrial Science and Technology. The focus of the AIST laboratories is concentrated on R&D programs judged to be capable of raising the level of Japan's technology in four main ways:

1. nurture new leading-edge technology that will lay the basis for future technical innovation
2. establish basic technical standards
3. meet the society's needs for earthquake prediction, pollution prevention, and environmental preservation
4. embrace all basic or general research that is appropriate for a national research organization

NAIR was founded in January 1993 with an objective of pursuing interdisciplinary research themes covering fundamental and frontier areas of industrial science. The institute is dedicated to the creation of international intellectual properties in broad fields of basic and strategic R&D, where national funds are expected to play a positive role. NAIR is characterized by the tripartite collaboration of industrial, academic, and governmental sectors, as well as by international cooperation. It is portrayed as an innovative attempt to overcome institutional boundaries by bringing together scientists of diversified specialty—not only from research institutes under AIST and the Science and Technology Agency (STA), but also from universities and research organizations in the private sector—to engage in intensive joint research.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

NAIR had four main research projects at the time of the WTEC visit:

1. The Atom Technology Project. This project has as its goal the ultimate technology for manipulating atoms and molecules; it started in January 1993 and runs until March 2002; total budget is ¥25 billion.
2. Research on Cluster Science Project. The goal of this project was experimental and analysis of the character of clusters; it ran from January 1993 until March 1998; total budget was ¥1 billion.
3. Research on Bionic Design Project. The goal of this project was to advance understanding in cell and tissue engineering and molecular machines; it ran from January 1993 until March 1998; total budget was ¥1 billion.
4. Basic Research on Next Generation Optoelectronics. The goal of this project is large capacity optical memory; this is a new program with seed money first available in April 1996; start date appeared to be April 1998, running until March 2003; total budget in April 1996 was ¥80 million for defining program goals and directions.

In addition to the above projects, NAIR has carried out several two- to three-year feasibility studies since its formation in 1993. The Atom Technology Project is the subject of a separate review in the JRCAT site report (p. 256 of Appendix D). The remainder of this report will focus on the Research on Cluster Science Project.

Research on Cluster Science

Dr. Harutoshi Takeo, the Cluster Science Group Leader, greeted the WTEC panel and first presented an overview of the science projects in his group, then led the panel on a tour of the laboratories. The cluster group consists of about 30 researchers, with nine regular research staff members, seven staff members on assignment from other AIST institutes, one from a university, 9-11 postdoctoral fellows, of which seven or eight are foreigners, and two to three graduate students. To further broaden the perspectives of the Cluster Science Group, it organizes a yearly workshop to which it invites 15-20 outside researchers. Over the lifetime of the project over 90 outside scientists will have participated in and contributed to these workshops.

The Cluster Science Group’s research areas fall roughly into four areas:

1. clusters in collisionless environments (molecular beams)
2. clusters in liquid or solution
3. clusters stabilized on surfaces or in matrices
4. clusters stabilized in a nanocage such as a zeolite

In the collisionless environment the main activities are focused on probing the structure and reactivity of clusters under single collision conditions. The research facilities, which have been designed and built entirely from scratch since mid-1993, include a Fourier transform ion cyclotron resonance mass spectrometer with which cluster structures are studied via laser spectroscopy; cluster chemical reactivity is being probed through controlled introduction of various molecular species. A second apparatus, a cluster beam system, combines infrared pumping of molecular adsorption on clusters with resonantly enhanced multiphoton ionization techniques to interrogate cluster and molecular bonding. Bonding of aniline and aniline dimers to a variety of different molecules has been studied.

To study the properties of liquid clusters, an expansion liquid droplet source together with a time-of-flight mass spectrometer (reflectron mode) was built. Study of mixtures of water/ethanol solutions have shown an evolution from clusters consisting of mostly water molecules complexed with one or two ethanol molecules for high concentration of water in the mixture, to clusters consisting of mostly ethanol molecules complexed with one or two water molecules when the ethanol concentration in the mixture reaches 40% or more. Such studies allow fundamental intermolecular interactions of molecules in liquids to be investigated.

To probe the properties of clusters on supports, several sophisticated pieces of experimental apparatus were built. One especially impressive experiment uses a liquid metal source (heated crucible) to produce clusters that are deposited on a cryogenic substrate in order to stabilize them. The apparatus is interfaced with an X-ray source. The substrate with different cluster deposits is rotated in-situ, allowing X-ray determination of the structure to be investigated as a function of the metal type, the cluster size, the substrate material, and the temperature. Interestingly, gold clusters with size < 6 nm are found to have icosahedral structure and not the fcc structure of bulk gold. Upon warming the substrate, the clusters sinter and the development of the fcc structure can be followed as a function of temperature. Studies of gold-copper alloy clusters also show icosahedral structure for clusters less than about 6 nm. Several other metal and metal alloy systems will be examined.

To investigate the quantum properties of nanometer-sized materials, the Cluster Science Group is attempting to stabilize metal clusters in the channels of zeolites. Specifically they have put sodium into the channels of an LTA zeolite in the hopes of producing a quantum wire. The sodium-doped materials have been shown to exhibit photochromic behavior, exhibiting reversible darkening upon exposure to light. In contrast, potassium-doped zeolites investigated by another group exhibited ferromagnetic behavior.

One of the researchers has developed a terahertz spectrometer capable of probing molecular vibrations in the 15-30 cm^{-1} range. At the time of the WTEC visit, this spectrometer appeared ready to be applied to real problems.

CONCLUDING REMARKS

In the short time it has existed, the NAIR cluster group has put together some of the best approaches of any group in Japan to study fundamental science issues. They began with virtually no equipment in 1993 and have designed and built a series of sophisticated apparatuses, each focused on probing a specific fundamental issue of cluster science. The unfortunate event was the termination of this effort in March of 1998. In this particular instance, the researchers are just beginning to harvest the results of careful and thoughtful design of state-of-the-art equipment. In at least one instance the apparatus was just coming on line at the time of the panel's visit, and that particular scientist will have only a few months to generate data before termination of the program.

It was the WTEC panel's perception that several of the researchers (almost all fairly young) did not yet have positions to which they could move. Some of the older researchers obviously will be able to return to their sending organization, but several were hired directly into this project and had no ties to any outside organization. We were informed that each researcher will be allowed to keep his equipment in the new position, which is certainly good news, but "the termination of the program" was a theme that had certainly raised the anxiety level of many of the staff. The quality of the research and the novelty with which these young researchers have approached science could serve as a model for other groups in Japan; namely, the researchers were allowed (even encouraged) to identify interesting cluster science problems and then design experimental apparatus to probe these problems, rather than to just buy equipment. This appears to have born fruit, but the fruit may dry up before harvest can occur.

Site:	**NEC** **Electron Devices Laboratory** **34 Miyugaoka** **Tsukuba, Ibaraki 305, Japan** **Fax: (81) 298-56 6135**
Date Visited:	23 July 1997
WTEC:	H. Goronkin (report author), D. Cox, J. Mendel, H. Morishita, M.C. Roco, R.W. Siegel
Hosts:	Dr. Kohroh Kobayashi, General Manager, Fundamental Research Laboratories Dr. Jun'ichi Sone, Senior Manager, Advanced Device Research Lab Dr. Y. Ochiai, Manager, Advanced Device Research Lab Dr. K. Tanaguchi, Manager, Exploratory Research Lab

BACKGROUND

Funding:	1% of NEC's sales go to its Corporate Research Laboratory (including the Fundamental Research Laboratories) 70% of funding is from the corporate level 30% is contract funding from business groups 15% of funding for Fundamental Research Laboratories is from business groups and national projects
Targeting:	Business group R&D, from three to five years Fundamental R&D Labs, from five to ten years
Staffing and Foci of NEC Labs:	Tsukuba: 300 (devices, materials, fundamental orientation) Kawasaki: 1,100 (computer and communication systems, software, and components) Princeton: 50-60 (computer science and physical science) Berlin, Bonn: (computers and communications software for parallel computers and ATM transmission technologies)

RESEARCH AND DEVELOPMENT HIGHLIGHTS

K. Taniguchi—Si, Ge, C Clusters

- the Exploratory Research Lab has synthesized buckyball magic numbers of 20, 24, 46, and 60 and has achieved >100
- change bonding from van der Walls to covalent by changing number of atoms in the ball
- doping provides conductivity and superconductivity
- need ionized Si or Ge; quench to remove electron and form 20 or 24 atom cages
- modify substrate to form clusters by adding electrons by doping, ion implantation, e-beam
- critical temperature for silicon cages is 6-8 K

Y. Ochiai—Nanofabrication

The Goal of the Advanced Devices Research Lab is 10 nm scale lithography using e-beam. It needs a capability by 2007 for manufacturing 16 Gbit DRAMs. Previous work on short gates includes 100 nm in 1987, 45 nm in 1993 using a 50 keV field emitter beam having less than 5 nm beam diameter at 100 pA; and 40 nm in 1997.

The lab is using Tox = 3.5 nm and is working on 1 nm SiO_2. Although tunneling will exist, it is believed that the small area of the gate oxide will limit gate current to a negligible fraction of the channel current.

W/L scaling is not maintained at 2:1.

The lab developed an e-beam resist (Calixarene, molecular weight 1,000) for the 10 nm project in which resolution is limited by the six benzene ring length to 6 nm; 10 nm lines show smooth edges and regular spaces. The resist was licensed to other companies for commercialization.

Atom Beam Holography

Starting with a Ne discharge, the neon momentum is decreased and the atoms are trapped in a laser beam. The Ne atoms are allowed to fall under gravitational attraction and they pass through a hologram plate before dropping onto a microchannel plate, where they excite an image. The large mass of Ne compared to electrons provides a large increase in resolution. According to quantum mechanics, the wave of a single Ne atom can pass through thousands of holographic channels simultaneously where it is diffracted and then recombined to form images on the microchannel plate. It is hoped that this can be used for future 1 nm lithography. It currently takes seven hours to form an image. This project began in 1995 in collaboration with the University of Tokyo.

Jun'ichi Sone—Nanoelectronics

Encouraged by Advanced Device Lab's success with e-beam lithography using Calixarene resists to obtain 10 nm features, various device structures become possible. The Lab's goal is to look for the classical-quantum crossover in MOSFET structures. There are many potential problems, including source-drain tunneling (S-D) and tunneling through the gate insulator. An EJ MOSFET (electrically variable junction MOSFET) was fabricated with gate lengths from 134 nm to 32 nm. A second gate located over the channel control gate was used to modulate the resistance of the source and drain virtual access regions. Satisfactory saturating characteristics were obtained down to 32 nm. At 32 nm, short channel effects were observed; however, no S-D tunneling was observed. At this writing, a 15 nm gate was achieved but results were not reported. It is hoped that when quantum effects are observed, useful novel devices can be made.

The advanced e-beam lithography with PMMA resist was used to fabricate a metallic single-electron transistor using $Al/Al_2O_3/Al$ island/Al_2O_3/Al. The process involves opening a 20 nm window between source and drain. The Al is oxidided to form Al_2O_3 , and Al is deposited in the window to form the island region. Extremely reproducible drain current peaks as a function of gate voltage were obtained. Unlike semiconductor SETs, for example, where the peaks are of uneven height, the lack of depletion and charging of defects provides uniform heights in the metallic system. It is believed that 10 nm islands could provide room temperature operation.

CONCLUDING REMARKS

NEC's Electron Devices Laboratory is one of the top labs in the world in nanoelectronics. This lab seems to be able to quickly start new programs in promising areas and to change direction when fundamental obstacles block the path to progress. The Atom Beam Holography and the 10 nm gate projects are at the leading edge. The lab appears to be clear in its understanding of how its research fits into future company needs and how the research must be directed to produce world-leading results.

Site: **National Industrial Research Institute of Nagoya (NIRIN)**
1 Chome Hirate, Kitaku
Nagoya 462, Japan
Fax: (81) 52911 1661

Date Visited: 25 July 1997

WTEC: J. Mendel (report author), D.M. Cox, C. Koch, H. Morishita, R.W. Siegel

Hosts: Dr. Shuzo Kanzaki, Chief Senior Researcher
Dr. Mutsuo Sando, Research Manager
Dr. Sakae Tanemura

BACKGROUND

The National Industrial Research Institute of Nagoya (NIRIN) has as its mission to carry out advanced materials research on ceramics, metals, composites, and related materials. Established in 1952, its main research field is material science and technology. There is close cooperation with domestic and global universities; there are also efforts to interface with other national research institutes.

Within Japan's National Industrial Research Institutes (NIRI) there are six major technical departments. In 1996, the annual budget for NIRI was $92 million (US). Total staff is 220 who participate in the Institute. For this visit, the WTEC panel focused on the area of synergy ceramics and materials.

In the area of synergy ceramics, the emphasis is on structural control for improving a specific property of a given material. Here there is effort to simultaneously control structural elements at every stage (from atomic scale to the macro scale). This approach is referred to as "hyperorganized structure control." In the area of synergy ceramics, there are a total of 30-35 people involved in the investigation of ceramics and metals. Size can be classified into four major categories for creating superior ceramic materials: (1) atomic and molecular scale, (2) nanoscale, (3) microscale, and (4) macroscale. In the hyperorganized approach to structure control, effort is made to harmonize and trade off functions, such as strength and toughness or electrical conductivity and stress sensitivity. In 1994, the synergy ceramics project was launched to foster collaboration among national research laboratories, universities, and industries. Part of the program is under the sponsorship of the New Energy and Industrial Development Organization

(NEDO) and is entrusted to the Fine Ceramics Research Association (FCRA).

The Synergy Ceramics Project is divided into *core research* and *satellite research* projects. Core research is being carried out at NIRIN and at the Synergy Ceramics Laboratory located in the Japan Fine Ceramic Center (JFCC) by researchers from FCRA, NIRIN, and several national universities. Satellite research is being carried out by 12 industrial organizations participating in the FCRA and by the Osaka and Kyushu National Research Institutes.

The projects that the WTEC panel were introduced to constitute only a portion of the core research. There are also many other topics being pursued as part of the Synergy Ceramics program.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Specific projects for synergy ceramics include the following:

1. alumina ceramics containing lanthanum oxide (La_2O_3)
2. alumina ceramics doped with SiO_2
3. alumina ceramics doped with both La_2O_3 and SiO_2 producing anisotropic grain growth of Al_2O_3 and in situ plate growth of La_2O_3
4. scaling of Si_3N_4 with Y_2O_3 and SiO_2; thermal conductivity values of SiN_4 are dependent on the processes of scaling and casting to improve strength, toughness, and Young's modulus
5. nanoporous silica films with one-dimensional throughput channels of 10-20 nm; high temperature oxides of Fe_2SiO_4 were prepared for evaluation as molecular sieves and particulate filters
6. preparation of submicron emulsions of Al_2O_3, surfactant and water; here, a silica coating is deposited on alumina powder; this coating makes the alumina surface negative over a broad pH range

EQUIPMENT

1. ISO pressing (12 tons/cm^2)
2. Ceramic furnaces
3. Superplasticity measurement device
4. High resolution TEM

FUTURE DIRECTIONS

The final year for this five-year program on synergy ceramics is 1998. It is anticipated that this program will continue in the pursuit of the synthesis of nanoporous materials for absorbing oil and identified particulates; the preparation ligands include ferrous materials such as ferrous disilicate; also of interest is the synthesis of ceramic materials with polymers that have low coefficient of friction similar to teflon.

RESPONSE TO WTEC QUESTIONNAIRE

Attached below are discussions on cluster engineering by Dr. Sakae Tanemura in response to the technical questions posed by the WTEC panel before the visit.

NIRIN's Research Activities on "Cluster Engineering" by Prof. Dr. Sakae Tanemura

Scientific Drivers

Those important to cluster engineering are as follows: new phenomena (cluster and surface interaction in both soft and hard collision cases; cluster coalescence and/or diffusion on the surface; solid state properties of assembled and/or embedded clusters).

Applications

Cluster itself is nanoscale material and shows the size-dependent quantum effect. If we can use a size-controlled cluster as a building block for nanostructure fabrication on a surface, we can fabricate new types of electronics (multiemitter-type resonance transistor, multitunnel junctions, and new magnetic devices having multivalued recordings with superhigh density). We will accomplish this by the combination of any materials and generally any substrates. "Cluster engineering" will help to break through some of the present difficulties faced by silicon technologies for nanostructures and will be a promising complement to silicon technologies.

Critical Parameters to Control

To move a high density size controlled cluster beam from the source to another vacuum vessel for deposition (for deposition by soft landing and/or hard collision); to identify a cluster source; and deal with cooling and filtration will require specific knowledge for installation to operate effectively.

To realize soft landing and/or hard collision deposition of clusters on a substrate, and to have ion optics to accelerate and deaccelerate ionized clusters will require specific designing skill.

To control the assembled parameters (parameters to control self-diffusion, migration and/or coalescence of deposited clusters, as well as the surface crystallinity of the substrate), including introduction of regular steps and/or kinks and termination of crystal bonds of surface atoms, will require extensive systematic research.

Current Status

These investigations have just begun with the cluster groups in Japan, the United States, and Europe, and the work is at a fundamental stage. Rapid progress will be expected within three to five years if certain research resources are available.

Time Scale to Completion and Manufacturability

It is difficult to estimate the time scale for ultimate application. This will be very much affected by the nanoscale requirements by semiconductor and memory industries. We must identify needs for large capacity and high speed memory requiring relatively small amounts of power.

R&D Philosophy

Our philosophy, directions, and basic concept are described in published brochures.

Overall Japanese R&D Activities on Cluster Engineering

I don’t know the overall R&D of nanotechnology throughout Japan. The definition of nanotechnology should be defined clearly. As far as I am concerned with cluster engineering in Japan, here are the other leading laboratories and/or persons working in this area:

1. JRCAT and NAIR (AIST, MITI) at Tsukuba: Atom Technologies group, particularly Dr. Y. Kanayama, (“Atom Technologies” project is a typical national project on nanostructures and being well funded by AIST, MITI)
2. Metal & Inorganic Material Institute, Tohoku Univ. at Sendai: Profs. K. Suzuki, K. Sumiyama and A. Kasuya. They are funded by “Strategic

Fundamental Research Fund" of Science & Technology Agency (STA) as three-year projects of about $2.5 million.

3. Ion Engineering Research Laboratory, Kyoto Univ. at Kyoto, Prof. I. Yamada and Dr. Z. Matsuo. Dr. Z. Matsuo is doing research on argon-cluster sputtering (no data for funding).
4. Cluster Lab., Toyota Inst. of Tech. at Ichikawa, Chiba, Prof. T. Kondow. The funding is given by the Kompon (Fundamental & Generic) Laboratory of Nippon Denso Co.
5. Chemistry Dept., Faculty of Science & Technology, Keio Univ., Prof. K. Kaya (no data for funding).

Educational Initiatives

All occur in the above-mentioned universities. I have already supervised my postgraduate student on cluster deposition.

NIRIN has already inaugurated international cooperation work on Cluster Engineering with Frei University, Department of Physical Chemistry, Berlin, Prof. Woeste's lab (experiments); and with Wien Technical University, Department of General Physics, Wien, Prof. G. Betz (MD simulation of cluster impact).

We welcome international cooperation on any subject related to cluster engineering.

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Date Visited: 23 July 1997

WTEC: C. Koch (report author), E. Hu, D. Shaw, C. Uyehara

Hosts: Dr. Masatoshi Okada, Director General
Dr. Mikihiko Kobayashi
Dr. I. Nakatani
Dr. N. Koguchi
Dr. M. Murayama
Dr. W. T. Reynolds
Dr. M. Ohnuma
Masatoshi Saito

BACKGROUND

The WTEC panel's host at the National Research Institute for Metals (NRIM) was Dr. Masatoshi Okada, Director General of NRIM, and the panel had presentations/discussions with Drs. M. Kobayashi, I. Nakatani, N. Koguchi, M. Murayama, W. T. Reynolds, and M. Ohnuma.

NRIM is a national laboratory devoted to the development and improvement of new and advanced metallic (and other) materials. It is funded by the Science and Technology Agency (STA). There are about 330 researchers out of a total staff of 415 people and an annual budget of about $100 million.

We were greeted by Dr. Masatoshi Okada, who then described his organization. The laboratory can be divided into four major parts: (1) research in advanced physical field (high magnetic fields, high resolution beams, extreme high vacuum), (2) research for materials science, (3) research for materials development, and (4) social-needs-oriented research. Researchers in various areas related to nanostructured materials presented descriptions of their research.

RESEARCH AND DEVEOPMENT HIGHLIGHTS

Dr. M. Kobayashi described his work on particle assemblage. At present this work is focused on micron-scale particles (~ 5 µm particles) and toward the preparation of "smart" materials. Particles are assembled by electrostatic force by several methods involving, for example, the atom probe or electrostatic patterning by electron beams with particles attracted to the patterned regions. Examples of materials include SiO_2 particle assemblages for gas (e.g., CO) sensors and Ni-base magnetostrictive particles for actuators.

Dr. I. Nakatani has a program involved with research on quantum magnetic properties. Studies involve magnetic substances with sizes of around (a) 100 nm, (b) 10 nm, and (c) 1 nm in dimension.

a) A novel reactive-ion etching method was developed and applied to producing ferromagnetic Fe-Ni thin wire arrays with 250 nm width and spacing.
b) Magnetic relaxation phenomena of iron nitride or cobalt ferrofluids were studied. These are colloidal 10 nm diameter ferromagnetic particles. The relationship between the viscosities of the magnetic fluids and volume fractions of solid particles was determined. It was stated that these ferrofluids possess the highest performance achieved in the world.
c) Giant magnetoresistance (GMR) was observed for 2 nm Fe particles embedded in SiO_2 or MgF_2. The GMR effect is due to spin-polarized electrons tunneling between the Fe particles.

Dr. N. Koguchi described his group's work on direct formation of GaAs/AlGaAs quantum dots by droplet epitaxy. The process consists of forming Ga droplets on the inert S-terminated AlGaAs substrate and reacting the droplets with As to produce GaAs microcrystals. First, a molecular beam of Ga is put on the substrate, followed by an As molecular beam. About 10 nm GaAs particles are formed. The photoluminescence of these structures is being studied.

Dr. M. Murayama and Dr. W.T. Reynolds (on sabbatical from VPI) described their studies of the microstructure of a variety of structural materials with nanoscale features. Included in their studies are fine atomic clusters in Al-base alloys in which clusters not resolvable with high resolution electron microscopy were revealed by special tomographic three-dimensional atom probes. NRIM has two of the three existing in the world. All materials they study with the atom probe are nanostructured, including

- magnetic materials — Co–12Cr–2Ta thin films
Fe-Zr-B amorphous/nc structures
- structural materials — steels (e.g., piano wire)
high strength Al-base alloys
(from A. Inoue's group at Tohoku University)

The piano wire—Fe–0.8%C—with a pearlitic structure-after strains of 4.0 assumes a nanocrystalline structure with 5 nm carbide particles, along with some amorphous regions.

Dr. M. Ohnumo described studies of GMR behavior in Co-Al-O granular thin films. This work is in collaboration with H. Fujimori from Tohoku University.

A new thrust of NRIM is enhanced cooperative programs with industry and universities, and with international programs. NRIM is designated as a Center of Excellence and is charged with development of state-of-the-art facilities for extreme high vacuum, high resolution beams, and high magnetic fields.

Site: **Osaka National Research Institute (ONRI)**
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Date Visited: 24 July 1997

WTEC: D.M. Cox (report author), C. Koch, J. Mendel, H. Morishita, R.W. Siegel

Hosts: Dr. Masatake Haruta, Chief Senior Researcher;
Head, Interdisciplinary Basic Research Section
E-mail: haruta@onri.go.jp
Dr. S. Tsubota
Dr. M. Okumura
Dr. Cunningham
Dr. Ando
Dr. Kohei Fukumi
Dr. Teruo Kodama, Director General of ONRI
Dr. Noboru Wakabayashi, Senior Officer for Research Planning

BACKGROUND

This WTEC site visit was hosted by Dr. Masatake Haruta, the Chief Senior Researcher at Osaka National Research Institute (ONRI), who presented an excellent overview of the AIST laboratories under MITI. ONRI is one of 15 national laboratories, of which 8 are located in Tsukuba. ONRI, founded in 1918, is the fourth oldest research institute of MITI. At ONRI there are five major research departments and one research section:

- Department for Energy Conversion
- Department of Energy and the Environment
- Department of Optical Materials
- Department of Materials Physics
- Department of Organic Materials
- Interdisciplinary Basic Research Section

These research departments focus on three primary areas: (1) energy related materials, (2) optical materials, and (3) fundamental research. The major components of energy related materials are energy storage using new battery technology; molten carbonate fuel cells; production, storage, transportation, and application of hydrogen energy; and catalysis. In optical materials the focus is on nonlinear optical materials and application of optical measurements. In fundamental research the focus is on thin film and ion beam technology, material design and characterization, and bioengineering of molecular complexes of peptides.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

ONRI is very proud of its history of contributions to industry, with several major inventions, discoveries, and developments in the labs at Osaka. Four of these are as follows:

1. polyacrylonitrile (PAN)-based carbon fibers, which are used as carbon fiber reinforcements for plastics used in golf club shafts and fishing rods, as well as for aerospace applications
2. transparent conductive films of indium oxide (and tin oxide) via vacuum deposition, which advanced liquid crystal technology; the transparent conductive films are also used commercially as anti-icing coatings and have been applied to windshields of the Tohoku-Shinkansen bullet trains
3. inorganic spherical microcapsules with porous walls, with applications in cosmetics and deodorants
4. the discovery that nanosized gold catalysts have specific catalytic properties useful for odor removal, specifically for rest rooms; this work is a recent invention from Dr. Haruta's group

Dr. Haruta, our host, in addition to his responsibilities as Chief Senior Researcher at ONRI, is head of the Interdisciplinary Basic Research Section, which was founded in 1994 as a new research section for basic studies, with a primary aim to provide fundamental knowledge to the science world.

The technical update was provided by Dr. Haruta plus several other members of his group, Drs. Tsubota, Okunura, Cunningham, Ando, and Fukumi. The work on "gold catalysts" is a major focus for ongoing research and has led to the discovery that supported gold catalysts exhibit unique catalytic properties only in the case where the gold particles are nanoscale and highly dispersed (gold particles on the order of 1-5 nm in diameter supported on metal oxides such as TiO_2).

S. Tsubota and M. Okumura described catalyst preparation techniques, characterization, and present understanding of the behavior of these materials as a function of particle size. Specifically, the particle size effects have been examined as a function of (a) the pH of the initial Au solution, (b) the effect of calcining temperature on the TiO_2 supports, (c) comparison of results using different synthesis techniques and parametric studies to optimize the catalyst fabrication, and (d) the wt% of Au loading.

The characteristic nature of the gold catalyst was the main topic of the science presentations from Dr. Haruta and members of his staff. This included evidence for the structure-sensitive character of the gold catalysts, namely, the strong dependence on particle size, type of support material, and the interface structure of the Au catalyst with the support. Gold catalysts have unique behavior, being active at low temperature. For example, CO oxidation occurs on nanoscale gold catalysts at temperatures as low as -70°C. In addition, the gold catalysts are found to exhibit very high selectivity for partial oxidation reactions, such as oxidation of propylene to propylene oxide with 100% selectivity at 50°C as well as near room temperature reduction of nitric oxide. A key scientific finding is the sensitive role that H_2O plays in activating the gold catalytic behavior. Similar results with Pd and Pt catalysts show effectively no propylene oxide yield, but give about 100% conversion to propane. The fundamental work on gold catalysts has led to "odor eaters" for the bathroom, a recent commercialization.

In addition to the ongoing studies on gold catalysts, there is a significant effort to apply the learning from the gold system to other catalyst systems, using, for example, Pt- or Pd-based catalysts with the expectation that particle size effects will lead to novel materials with highly specific functionality.

In addition to the catalysis work, the Basic Research Section also has efforts in developing optical gas sensors, and in studies of the unusual nonlinear optical properties of gold nanoparticles. The use of sputtered gold or nanoparticle gold colloids deposited on transition metal oxide surfaces has produced surfaces for which selective adsorption of H_2 and CO gases can be detected. The use of entirely optical techniques for selective detection of H_2 was being promoted, since such detection would eliminate the possibility of fire ignition or explosion in H_2 atmospheres. Dr. Ando summarized the optical gas sensor work as follows:

- Au nanoparticles on nickel oxide show enhanced selectively to both CO and H_2
- Au nanoparticles on copper oxide show large selectivity and sensitivity to CO
- Au nanoparticles on cobalt oxide show two effects:
  - Enhanced selectivity to H_2 at the plasmon band of Au
  - Decreased absorbance (selectivity) to both CO and H_2 away from the Au plasmon center frequency.

The results open the possibility for strictly optical recognition of H_2 and CO.

Dr. Fukumi showed that nanoscale gold colloids dispersed in glasses exhibit novel nonlinear optical properties. The materials are produced by ion implantation of Au^+ into silica glass. The Au+ ion energy is 1.5 MeV with densities of 10^{16}-10^{17} Au^+ ions/cm^2. Characterization by TEM showed the average particle size was 8.6 nm diameter. In these materials, the third order nonlinear susceptibility χ^3 was measured to be 1.2 x 10^{-7} esu, about four orders of magnitude higher than that obtained by a melting method used by others to produce the gold/glass system.

Following the technical presentations, the WTEC team enjoyed a lunch that Dr. Haruta had kindly arranged with the Director General of ONRI, Dr. Teruo Kodama, and Dr. Noboru Wakabayashi, the senior officer for research planning. After lunch the team had a tour of the lab facilities of the Interdisciplinary Basic Research Section. From these interactions we learned that funding for the National Laboratory at Osaka increased by 16% in 1996, but simultaneously, the permanent staff is decreasing. The decrease in permanent staff is somewhat compensated by the increase in (mostly) foreign postdoctoral support to the 30-40 person level.

The lab facilities for the Basic Science Section are impressive, consisting of several catalyst testing units and a special testing unit with all stainless steel surfaces that have been chromium oxide-coated to allow water vapor levels to be reduced to < 10 ppb. This is the only unit in the world with this capability, which has allowed this group to carefully isolate the role of water vapor in the catalytic reactions. Recent funding has allowed purchase of a new high resolution TEM (~$1.3 million), and a new sophisticated surface science apparatus (>$1 million) which at the time of the WTEC visit had been ordered but not yet delivered. The new equipment is to be used to better understand the differences and similarities of surface reactions occurring at low pressure under UHV conditions and those occurring in the higher pressure catalytic reactions carried out under actual processing conditions.

Site: **Osaka University**
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Date Visited: 24 July 1997

WTEC: J. Mendel (report author), D.M. Cox, C. Koch, H. Morishita, R.W. Siegel

Host: Prof. Koichi Niihara, Director

BACKGROUND

The Institute of Scientific and Industrial Research was founded in 1939 as part of Osaka University. Its whole purpose is to study scientific principles necessary for industry to make progress in the fields of electronics, computer science, and metallic and inorganic materials, as well as other disciplines in biochemistry and radiation science. In 1995 the Institute was restructured into 6 divisions and 24 departments. The six divisions are (1) Quantum Engineering; (2) Advanced Materials Science and Technology; (3) Organic Molecular Science; (4) Intelligent Systems Science; (5) Biological Science; and (6) Quantum Beam Science and Technology.

The Institute's budget in 1996 was $25 million. For the area of Intermaterials, the budget amounted to $4 million plus grants from companies. For the Department of Structure Ceramic Materials, there are a total of 25 individuals supporting this technology. Professor Niihara, who heads this department, had been at the institute for eight years. Eighty per cent of the students work on ceramics, both functional and structural, and 20% are involved with metals and polymers.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

The main focus for programs within Structure Ceramic Materials is ceramic-based nanocomposites prepared by sintering methods. There is special emphasis placed on understanding the relationships between the nanostructure of materials and their mechanical properties. Ceramic nanocomposites can be divided into intragranular, intergranular, and nano/nano composites. Intragranular and intergranular nanocomposites, even at elevated temperatures, result in remarkably improved mechanical properties, including (1) fracture toughness, (2) abrasive and cutting performance, (3) fracture mode, (4) fracture strength, (5) maximum operating temperature, and (6) creep resistance. As an example, toughness may increase 1.5 to 4 times in the Al_2O_3/SiC system. Hybridization of micro- and nanocomposites using fiber-reinforced components results in toughness improvements at higher temperatures.

Specific Classifications

Multifunctional ceramics, then, can have some specific classifications:

1. micro-nano composites with enhanced toughness (Al_2O_3/SiC)
2. hard matrix/soft dispersion nanocomposites (Si_3/N_4/BN)
3. soft matrix/hard dispersion nanocomposites
4. structural ceramics
5. nanopore composites as future targets

Preparation

The process for preparing these ceramic materials involves a sintering reaction where the challenge is to keep different size particles uniformly dispersed to prevent nonuniform distribution.

Wet ball milling is also used, where materials like Si_3N_4 are mixed with Al_2O_3, Y_2O_3, H_3BO_3, and urea. After ball milling, the material is dried and subjected to hydrogen reduction. Such processes have yielded properties like high strength, excellent thermal shock resistance, good chemical inertness, and easy machinability similar to metals. Addition of chrome oxide has also yielded improvements in Young's modulus and fracture strength.

Although the institute has no formal process for patents, the work has resulted in the granting of 35 patents from this ceramic technology. Collaboration with the Massachusetts Institute of Technology and laboratories in Germany is ongoing.

Equipment

A tour of laboratory facilities showed a wide range of processing and characterization equipment. Included are (1) ceramic ovens, (2) Instron with filament-winding equipment (3) X-ray diffractometer with temperature range to 2000^{o}C, (4) laser Raman, (5) hot isostatic press, (6) SEM, (7) AFM, (8) nano-indentor, and (9) spark plasma sintering systems.

Site: **RIKEN (Institute of Physical and Chemical Research)**
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Date Visited: 22 July 1997

WTEC: E. Hu (report author)

Host: Dr. Aoyagi, Coordinator, Frontier Research Program; Chief, Semiconductor Laboratory
Dr. Katsuhiko Fujita, Exotic Nano Materials Group
Dr. Takashi Isoshima, Researcher, Biopolymer Physics Lab.
Dr. Hideo Yabuki
Yoshiro Miki, Director of the Frontier Research Program Division and the Brain Science Planning Office

BACKGROUND

The Frontier Research Program was set up within the Institute of Physical and Chemical Research (RIKEN) within the Science and Technology Administration to be a more flexible program emphasizing

- multidisciplinarity
- flexibility, obtained by recruiting researchers with the proper expertise, working under one-year contracts that can be extended (average age of the researchers is 35)
- international participation, with non-Japanese team leaders; 1/3 of the participants are from overseas
- active recruitment of young researchers
- external evaluation by world-class scientists
- forum to create new ideas

All programs have a fixed lifetime of eight years, extendible, with a mid-program review. The Frontier Materials Research program that the WTEC team visited was in Phase II of its activities.

Within the Frontier Materials Research Program were three subareas: (1) the Laboratory for Nano-Electronics Materials (Sugano), (2) the Laboratory for Nano-Photonics Materials (Sasabe), and (3) The Laboratory for Exotic Nano Materials (Knoll). The emphasis is on basic research, rather than on applications (this was explicitly stated).

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Dr. Aoyagi gave the WTEC team an introduction to some of his team's research activities.

Quantum wire growth: they used a technique similar to that developed by Kapon for the growth of (primarily) GaAs/AlGaAs and GaP/AlGaP quantum wires. The attempt was to improve that process and gain better control of the growth process, with a higher selectivity of incorporation, using the fact that the growth rates on the (111)A plane is minimal to zero. Measurements were done in a 40 T magnetic field; the researchers expected to observe a diamagnetic shift in the luminescence peak under the high field conditions, and obtained 123 $\mu eV/T^2$ for the LH transition and 210 $\mu eV/T^2$ for the HH transition. These are far larger shifts than expected (110 $\mu eV/T^2$ for bulk and 20 $\mu eV/T^2$ for 2-D systems). Aoyagi attributes the discrepancy to the influence of the interaction of the electrons in the wire with the adjacent impurities.

Si nanostructure formation: these studies began with amorphous silicon deposited onto Si substrates and annealed in a hydrogen or nitrogen ambient. The result was the formation of Si nanocrystals, ~ 7 nm in size, embedded within an amorphous matrix. Emission in the blue was observed, with about 10^{-5} stated efficiency. Emission at 420 nm and 380 nm was observed. Simulations have been carried out to look at the effects of confinement on the relative regions of the amorphous and crystalline areas (Figure D.8).

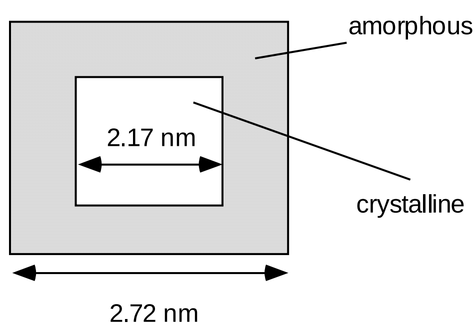

Figure D.8. Effects of confinement on the relative regions of the amorphous and crystalline areas.

GaN dot formation: dot formation is attempted on a nearly lattice-matched substrate: GaN on AlGaN (thin buffer layer, grown on SiC, ~ 10^{-7} defects/cm^2). Growth is believed to proceed by step-flow. In order to promote dot formation (without the influence of strain), researchers chose to *control the surface energy*, by using a monolayer of silicon as a surfactant (this has been published in APL). They have achieved stimulated emission in these dots, with a density of greater than 10^9/cm^2.

Transport: Dr. Aoyagi showed the WTEC team quantum dots formed by split gate structures, with a separate gate that allowed coupling between 2 dots. He observed interference fringes in the I-V, indicative of coupling, measurements taken at 10 mK. He also showed magnetoCoulomb oscillations, using the magnetic field rather than a gate to alter the interactions (Figure D.9).

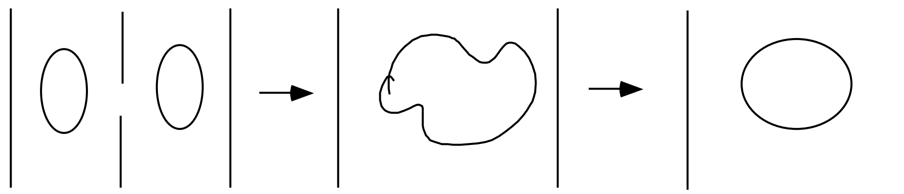

Figure D.9. MagnetoCoulomb oscillations using the magnetic field.

Dr. Aoyagi then took us for a brief tour of various labs in his area: a transport lab with three cryostats, an He 3/4 dilution refrigerator, and high field magnets (8 T); a JEOL e-beam writer, MOCVD capabilities (MBE was elsewhere), analysis lab with focused ion beam and photoluminescence spectroscopy.

- The WTEC team was then provided with some overviews of the research in the Exotic Nano Materials group. Dr. Katsuhiko Fujita discussed some of the projects within this group, headed by Dr. Wolfgang Knoll. He described a supramolecular architecture, building from a substrate to a metal layer, to a biological interface to proteins. Dr. Fujita described a project in which fabricated gratings of various periods were used to facilitate studies on the motility and growth of hippocampal neurons. Another project involved the integration of neurons with transistors, to be used as in-situ recording devices. Laboratory support included capabilities for the synthesis of biopolymers, as well as characterization facilities, including scanning tunneling microscopy (atmospheric and ultrahigh vacuum), and atomic force microscopy. A surface plasmon resonance microscope and a near field optical microscopy facility are also being developed.

Dr. Takashi Isoshima, a researcher in the Biopolymer Physics Lab (degree from Tokyo University), then described some of the experiments involving polymers for optical devices: ultrafast optical switching, low power consumption photorefractives. This group carries out its own polymer synthesis, molecular design, and modification, in order to enhance optical properties such as nonlinearity and absorption. The goal is to synthesize multicomponent, photorefractive materials with capabilities in electrooptic coefficient, photoconductivity, etc. He showed us an impressive optical characterization lab: subpicosecond systems, a time-resolved fluorescence setup (100 fs), three optical benches, and optical fiber devices for ultrafast multiplexing.

Dr. Hideo Yabuki then gave us a general overview of RIKEN, its history and current mission. RIKEN is a semipublic corporation, receiving 95% of its funding from the Science and Technology Agency. It is believed that this semipublic status gives it more autonomy. There is extensive collaboration with universities (University of Tokyo, Tokyo Institute of Technology, and others), with a number of dual appointments and joint doctoral courses. RIKEN collaborates extensively on an international scale and has established a number of laboratories outside of Japan; the Rutherford Appleton Laboratory was the first overseas lab to be established.

Yoshiro Miki, the Director of the Frontier Research Program Division and the Brain Science Planning Office (he has been at STA, in Materials Research, and then at MITI on an excimer laser project), spoke of a new priority project: a brain research institute. Citing a research effort that is only 10% of that carried out in the United States, promoters of the brain research institute hope that this will help to bring "brain science" in Japan up to world-class levels. Miki also spoke of the disconnect between RIKEN and the universities in terms of identifying important research priorities; there is a 10-15 years lag between initiation of RIKEN priority programs and observation of changes in university programs.

EQUIPMENT

Various laboratory equipment included a synthesis lab, with Langmuir Trough, Brewster angle microscope, an analysis laboratory with two STMs, a UHV STM, and AFM. WTEC's hosts described the development of a surface plasmon resonance microscope (magnification limited), and a near field optical microscopy facility that is being built under the coordination of Dr. Ruggiero Micheletto (current resolution is 100 µm).

Site: **Tohoku University**
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Date Visited: 21 July 1997

WTEC: E. Hu, C. Koch, and D. Cox (report authors), L. Jelinski, M. Roco, R.W. Siegel, D. Shaw, C. Uyehara

Hosts: Prof. Kenji Suzuki, Director, Institute for Materials Research; E-mail: suzuki@snap8.imr.tohoku.ac.jp
Prof. Masayoshi Esashi, Department of Mechatronics & Precision Engineering
Prof. A. Inoue, Head, Nonequilibrium Materials Laboratory
Prof. H. Fujimori
Prof. Kenji Sumiyama
Dr. Changwu Hu
Dr. Elisabeth Kurtz
Dr. Darren Bagnall

BACKGROUND (Carl Koch)

Most of the WTEC team's visit to Tohoku University was focused on the Institute for Materials Research (IMR) which is directed by Professor Kenji Suzuki. IMR's historical roots go back to 1916; at first it was devoted to research on iron and steel. However, under the leadership of Professor Matsumoto it became a leading research laboratory in the 1970s and 1980s in the area of nonequilibrium processing techniques for producing metastable materials, in particular metallic glasses, an area in which it was a world leader. At present IMR is a large modern materials research center containing 26 research laboratories in which approximately 160 scientists, 120 technicians, 190 graduate students, and 70 visiting scientists carry out a variety of research projects. The major part of the financial support for the IMR is provided by the Ministry of Education, Science, Sports, and Culture (Monbusho). The specific groups in the IMR concerned with nanoparticles/ nanostructured materials that the panel visited are those of Professors K. Suzuki and K. Sumiyama (metallic nanocluster assemblies), Professor Kasuya (semiconductor nanocluster assemblies), Professor H. Fujimori (magnetic nanostructured materials), Professor A. Inoue (nanostructured bulk materials), and Professor T. Yao (semiconductor nanodevices). Brief descriptions of these research efforts are given below. In addition to visiting IMR, the WTEC team visited the Tohoku University laboratory of Professor Esashi in the Department of Machine Intelligence and Systems Engineering. Professor Esashi's research on micro/nano machines is also described.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Prof. M. Esashi (Lynn Jelinski)

Microsystems by Silicon Machining: This program at Tohoku University, under the direction of Prof. M. Esashi, is located on the "mountain" campus of Tohoku, about a 15-minute drive from the main campus. The program has five components and is staffed by 35 professionals. The components are:

- active catheter and piezoelectric films
- inertia measurement systems
- microactuators and thermal and fluidic micro systems
- ultrasensitive sensors and nanostructures
- semiconductor research institute

The professionals comprised postdoctoral fellows from a number of countries, resident staff, and employees of a number of companies, including Samsung, Ford, Hitachi, Asahi Optical, and Honda.

Prof. Esashi has been working in the area of microelectromechanical systems (MEMS) devices for the past 25 years and over that time built up a fairly sophisticated, albeit homemade, facility for producing MEMS devices and another facility for characterizing them. A number of biomedical devices have been produced over the years, including blood gas sensors, a 1 mm diameter, navigable catheter based on shape-memory alloy material, produced with an STM tip, using a heated silicon substrate.

In the past several years there have been major capital investments into the program, resulting in the building and equipping of a microfabrication facility and a separate nanofabrication facility.

The microfabrication facility, also called a Venture Business Laboratory, was constructed and outfitted with government money. Companies are encouraged to make use of the facilities. The names of 27 companies, most of them large and well known, were displayed in the entryway.

The microfabrication facility consisted of a 0.5 micron CMOS line for 2-inch wafers, and housed an impressive array of modern equipment, including He-Cd and Ar lasers for laser fabrication, and laser-induced CVD.

This facility was very heavily invested in etch equipment, which included a molecular beam etch station for fairly sophisticated controlled etching. There was room after room of characterization equipment, including field emission SEM, SIMS, an SEM for characterizing biological systems under water, and an in situ monitor. There was also highly specialized equipment, including an entire room devoted to sensor characterization, which housed an accelerometer tester that worked in vacuum and a position-sensitive device that also worked in vacuum.

The nanofabrication facility, a Class-1000 cleanroom, was about a year old. Like the microfabrication facility, it was equipped with an impressive array of new and sophisticated equipment, including an e-beam direct exposure system and a stepper/pattern generator. It is conservatively estimated that the facility cost $10 million.

There was also a nanodevice characterization room, including ultrahigh vacuum AFM, STM, STEM, and ESCA. An in situ infrared ellipsometer was available for characterization of epitaxial layers.

While the size scale of the micro- and nanomachines we learned about were larger than that covered in this report, two projects bear description:

1. Esashi and coworkers (Ono et al. 1997) described the use of an ultrahigh vacuum STM to produce a silicon nanowire via field evaporation of silicon. A gold STM tip was positioned over a clean silicon substrate, the later of which was held at 700°C. At an applied sample voltage of 5 V (10 nA tunneling current) for 15 min., with the tip positioned 6 Å above the surface, growth of the silicon nanowire could be monitored by in situ SEM. The diameter ranged between 20-150 nm and the length was about 3 mm. Electron diffraction patterns showed that the wire was silicon, with between 2 and 15 at.% gold on its surface. It is posited that the field evaporation of silicon is enhanced by the formation of an Au-Si eutectic on the substrate.
2. In other work, the group described a self-supported silicon nanostructure that had been fabricated on a silicon diaphragm (Hamanaka et al. 1997).

Prof. H. Fujimori (Carl Koch)

The focus of Professor Fujimori's group is on new developments in the field of magnetic materials. A major part of this effort is directed at nanocrystalline (nc) Fe-based soft magnetic materials. A major method of processing utilizes preparation of amorphous precursors by melt spinning or sputtering followed by partial crystallization of nc bcc Fe particles. The nc Fe particles provide high magnetic moments and, if < about 20 nm in diameter, exhibit small crystalline anisotropy and superior soft ferromagnetic properties. An example given is an Fe-base amorphous alloy produced by sputtering that contains Hf, Ta, C, which on crystallization gives 10 nm Fe particles whose grain boundaries are pinned by about 10 nm diameter carbide (e.g., $Fe_{80}Hf_8C_{12}$) particles, which stabilize the nm grain size up to elevated temperatures (~ 700°C). This material exhibits almost constant permeability μ', with frequency up to about 10 MHz while the μ" (imaginary, lossy) component rises at values between 1 and 10 MHz.

Another interesting topic involves preparation and property measurements of metal/nonmetal granular nc composites. Sputtering was used to form systems such as Fe/SiO_2, Co/Al_2O_3. As the oxygen concentration in the films increases, the electrical resistivity increases from metallic (10^1–10^2 μΩcm), to a ρ vs. T behavior with a ρ minimum with $\rho = 10^2$–10^3 μΩcm, to high resistivity (negative coefficient of ρ) with $\rho = 10^4$–10^{10} μΩcm. The low oxygen content composites show ferromagnetic behavior with high permeabilities—about double that of ferrites but with higher losses. A potential application is use as a high frequency inductor.

The oxygen-rich composites exhibit giant magnetoresistance (GMR). For example, the Co, Fe in Al_2O_3 provides an assembly of tiny tunneling junctions with $\Delta\rho/\rho_o$ about 7.8%.

Fujimori's magnetic materials program is expected to receive an additional $3.8 million in government funding for the next five years in a new program entitled, "Nanostructurally controlled spin dependent quantum effects and new electronics and magnetics." A goal is a one-electron spin memory.

Prof. A. Inoue (Carl Koch)

Professor Inoue's large group (41 persons) studies amorphous, quasi-crystalline, and nc materials. The nc materials are typically prepared by crystallization of amorphous precursors, which can be bulk amorphous alloys, ribbons or wires produced by melt spinning, or rapidly quenched powders produced by powder atomization methods. Mechanical tests on nc/amorphous alloys from bulk amorphous samples exhibit increased yield strengths but little elongation in tension—that is, behavior similar to amorphous alloys even though 60–70 vol.% of the material is crystalline. Mg-base alloys have been successfully studied in this regard.

The equipment for processing, material characterization, and property measurements in Inoue's laboratory is very impressive indeed, with most nonequilibrium processing tools, sophisticated characterization, and property measurement facilities available.

The innovative work on metastable materials Professor Inoue has carried on over the years cannot be praised too highly. He and his coworkers are responsible for a new class of soft ferromagnetic materials based on Fe-Zr-B compositions that consist of nanocrystalline bcc Fe particles in an amorphous matrix. These materials exhibit the lowest core losses at frequencies up to 400 Hz of any known material. They have also developed alloys based on Al or Mg, which are two-phase nanocrystalline and amorphous and which exhibit high strength, e.g., the Al alloys have more than double the strength of the strongest existing Al alloys, along with some ductility.

A major factor in his group is its close association with Japanese industry. This is illustrated by the fact that 20 of his 41-member group are employees of many companies, specially assigned to carry out research in his group.

Profs. K. Suzuki and K. Sumiyama (Don Cox)

Prof. Kenji Sumiyama and Dr. Changwu Hu gave highlights of some of the work being done in the areas of metallic nanocluster assemblies and work on fullerenes and carbon nanotubes, respectively. In the metallic nanocluster area the main focus is on developing different techniques for production of metallic clusters.

Prof. Sumiyama described five different techniques for production of metallic clusters that have been utilized by his group:

1. ionized cluster beam deposition
2. plasma sputtering with cluster aggregation
3. field emission of atoms from a metal (gold) tip
4. liquid metal ion source
5. laser ablation cluster source

For characterization their main tools are electron microscopes, e.g., SEM, FE-TEM, and STM examinations of clusters deposited on substrates. The primary use appears to be for evaluation of the cluster size and cluster size distribution from the various cluster production techniques. Every researcher appears to be well equipped, with each possessing electron microscopes for individual use. They reported plans to add electron holography capability to the field-emission TEM next year. In addition to use as cluster size and size distribution measurements, recent STM studies of selenium clusters deposited on HOPG were interpreted as the first evidence for six or eight metal atom rings covering an HOPG surface.

The ionized cluster beam apparatus is the most developed and was an early workhorse, with several publications reporting work using this source. More recently, a new plasma sputtering apparatus has been constructed over the last four years and has become the primary cluster synthesis apparatus at IMR. Drs. Suzuki and Sumiyama reported being able to produce clusters of smaller sizes and with narrower size distributions than was possible with the ionized cluster beam apparatus and are optimistic that this source can be scaled up for much larger production than currently feasible. For example, with the plasma sputtering apparatus, they reported production of chromium clusters with sizes ranging between 3-4 nm with about 10% variation in size. Previously, the average cluster size was about 8-9 nm, but with a larger variation in size. Optimization of the helium and argon gas mixtures used in the plasma sputtering have resulted in better control of the cluster size and cluster size distribution, according to Prof. Sumiyama. The laser ablation cluster source is now being developed for production of transition metal clusters. The other two techniques, field emission and liquid metal ion source, are not as versatile, being limited to materials that have relatively low melting points.

Dr. Changwu Hu (Don Cox)

Dr. Hu described the efforts at Tohoku in the area of fullerene and carbon nanotube production and characterization. Dr. Hu described three main items:

1. chemical reaction studies of C_{60} on Si(111)
2. polymerization of C_{60} and C_{84} by argon ion laser irradiation
3. production and characterization of single-walled carbon nanotubes

In (1), the chemical reaction of C_{60} on Si(111), C_{60} is deposited on Silicon(111) and then heated to 800°C. At 800°C STM shows that a monolayer of C_{60} in registry with the Si(111) surface is covering the surface. Upon further heating to 850°C, the C_{60} layer becomes disordered. Heating even further to 1100°C results in formation of SiC in the form of SiC clusters of about 50 nm diameter and 2-4 nm height. This technique is reported to be a novel low temperature route to SiC.

In (2) the fullerenes are observed by STM to polymerize upon irradiation by an Ar ion laser and form large (150 nm diameter) clusters. Additional studies showed that the STM pattern changed with changing bias voltage, suggesting some polymerization is induced by the STM electric fields.

Lastly, Dr. Hu reported recent results on characterization of nanotubes produced in the laboratory. The researchers report single-walled nanotube yields of 20-30%, and that the diameter of the single-walled nanotube depends on the metal used in their (metal catalyzed) production, e.g., nanotube radii of 0.5 nm, 0.65 nm, and 1.0 nm for Fe/Ni, Co, and La, respectively. Raman spectroscopy and STM are used to characterize the nanotube deposits. Attempts to interrogate the electronic structure have been unsuccessful thus far.

The overall picture is that this group at Tohoku is well equipped as far as the electron microscopy techniques are concerned and is primarily interested in developing larger scale production techniques for both metallic clusters and for carbon nanotubules. It was not clear what the ties to future technology development may be.

Prof. T. Yao's Lab: Drs. D. Bagnall and E. Kurtz (Evelyn Hu)

Dr. Takafumi Yao's general research goal is "to exploit new optoelectronic materials for the 21^{st} century." The WTEC team's visit to Professor Yao's laboratories was hosted by two postdocs working with him: Dr. Elisabeth Kurtz and Dr. Darren Bagnall. Drs. Kurtz and Bagnall are two of three foreign (JSPS) postdocs working within Dr. Yao's lab. (This laboratory is apparently one of three under Professor Yao's supervision; another one is located in Tsukuba). They described projects in the nanostructured growth of wide bandgap materials: ZnO and CdSe.

Dr. Bagnall spoke of *Plasma-Assisted MBE of ZnO for Blue-UV Emitters*. A plasma source of oxygen was used to assist the epitaxial growth of ZnO on sapphire substrates. Free exciton emission dominates at room temperature, and pulsed, optically-excited lasing was observed up to 500 K, with fairly large thresholds: 2.5 MW/cm^2. With the large amount of strain between ZnO and sapphire, it would not be surprising to observe nanostructure growth (e.g., islands). In fact, AFM traces showed evidence of pyramidal structure: this was *not* thought to be the basis of the excitonic emission. Bagnall hopes to grow quantum wells in this material structure.

Dr. Kurtz described the growth of self-organized quantum dots in the CdSe material system: (111)A ZnSe was grown on a GaAs substrate, and CdSe dot structures were subsequently nucleated on this surface. The (111)A surface was utilized because it provided a smooth, featureless surface. The dots had typical diameters of 47 nm, with a height/diameter ratio of 19%. There are some interesting differences in these dots compared to self-organized dots in the III-V materials, such as InAs/GaAs:

- They have less stability: the dot dimensions are not stable with time, due to Ostwald ripening.
- Under different growth conditions, the dot *sizes* do not change, although the densities do change. Typical densities range from $5\text{-}25(\mu m)^{-2}$ (using atomic layer epitaxy with either 1 or 3 cycles of growth). In the III-V materials, the dot diameter and dot density are usually coupled, i.e., one cannot change one parameter without having the other parameter also vary.

Both projects used cathodoluminescence, photoluminescence, and AFM measurements in their analysis. There was a lack of modeling effort complementing the experimental work of the group. There seemed to be access to a broad range of characterization tools within or external to the Yao group—such as near field scanning optical microscopy. The WTEC team was taken for tours of some of the Yao labs, which include five MBE stations, cathodoluminescence (CL), photoluminescence (PL), X-ray analysis, and a UHV STM.

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Hamanaka, H., T. Ono, and M. Esashi. 1997. Fabrication of self-supported Si nano-structure with STM. In *Proc. of IEEE, MEMS '97* (January), pp. 153-158.

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Yokohama 226, Japan
Tel: (81) 45-924 5759; Fax: (81) 45-924 5779

Date Visited: 21 July 1997

WTEC: L. Jelinski (report author), E. Hu, M.C. Roco, D. Shaw, C. Uyehara

Host: Professor Masuo Aizawa, Faculty of Bioscience and Biotechnology; E-mail: maizawa@bio.titech.ac.jp

BACKGROUND

The Tokyo Institute of Technology has two campuses, one at Tamachi and another at Nagatsuta. The Nagatsuta Campus is about 20 years old, and the Faculty of Bioscience and Biotechnology was moved there about six years ago.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Professor Aizawa, whose laboratory the WTEC team visited at the Tokyo Institute of Technology's Nagatsuta Campus, was the project leader of a ten-year national MITI project on bioelectronic devices. The project, which ended in 1995, involved eight electronics companies and two national labs for its initial five-year period. One of the electronics companies dropped out and did not participate in the second term. An example of the work performed in the project is that by Mitsubishi, which produced an artificial protein that binds an electron acceptor and electron donor.

It appears that much of what was accomplished in the MITI bioelectronics project was accomplished in Aizawa's laboratory (see below). He set out to answer the question, "Are biological systems ideal for molecular electronics or not?" Parts of the project that are being continued appear to be in the form of RIKEN's Brain Research Center. Formulation of ideas for somewhat related work is being carried out by the Intelligent Materials Forum, whose members are working to promote a national project in this area. (The president of the forum is Toshinori Takagi; Aizawa is the vice president.) The idea of intelligent materials is to incorporate sensing and transduction and information processing into the same materials. The idea of forming a “Nanospace Laboratory” was just coming together at the time of the WTEC visit.

Aizawa has been a world leader in bioelectronics. His review on molecular interfacing for protein molecular devices and neurodevices (Aizawa 1994) describes subjects such as the coupling of electron transfer proteins (e.g., glucose oxidase) to solid surfaces, conducting polymer wires that couple the enzyme to the surface, and electrically modulated activity of molecular-interfaced enzymes.

More recent work, not yet published at the time of the WTEC visit, involved developing methodology to orient antibodies on surfaces. The key to making this work was to genetically modify protein A, known to bind the non-antigen binding stalk of the “Y” of the antibody, so its C-terminal carried a cysteine. The modified protein A was then bound to a gold surface via the well-known alkylthiol/gold chemistry. The ability to control the orientation of proteins on the surface is a major step forward in the ability to use these systems for drug targets, biochemical purifications and separations, and for sensing and diagnostic applications.

In other experiments, liposome nanoparticles were engineered by coupling to phosphatidyl choline, a peptide corresponding to one antigen binding domain of an antibody (Kobatake et al. 1997). These nanoparticles were used as the basis for a new fluoroimmunoassay.

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Kobatake, E., H. Sasakura, T. Haruyama, M.-L. Laukkanen, K. Keinänen, and M. Aizawa. 1997. A fluoroimmunoassay based on immunoliposomes containing genetically engineered lipid-tagged antibody. *Analytical Chemistry* 69(7): 1295-1298.

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Fax: (81) 3-5689 7352

Date Visited: 22 July 1997

WTEC: D.T. Shaw (report author)

Hosts: Prof. H. Komiyama, Dept. of Chemical Systems Engineering
Dr. H.S. Zhou
Dr. Fumihiro Wakai, Professor, Center of Materials Design, Tokyo Institute of Technology, Yokohama

BACKGROUND

The University of Tokyo is the oldest and the most prestigious university in Japan. Prof. Komiyama belongs to the Department of Chemical Systems Engineering, which is one of three departments (the other two are the Department of Applied Chemistry and the Department of Chemistry and Biotechnology) in the Department of Chemical Engineering. His work on nanoparticles has focused on the synthesis and optical properties of nanocomposites of metal/organic, organic/metal, metal/semiconductor, and semiconductor/semiconductor particles. More recently, coated self-assembled nanoparticles have also been studied.

Overall, Prof. Komiyama's work on nanoparticles and nanoparticle structures has focused on fundamental studies of the effects of quantum confinement of heterostructured nanoparticles and nanoparticle structures. Prof. Komiyama's laboratory is extremely well equipped and has formed strong connections to other research laboratories both within and outside Japan. At the present time, all his research projects appear to be experimental. In fact, the last theoretical work was conducted in cooperation with Prof. Joseph W. Haus (Physics Department, Rensselaer Polytechnic Institute, RPI) who visited him for one year in 1992.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Dr. H.S. Zhou, who is now a researcher at the Electrotechnical Laboratory at Tsukuba City, showed me his work with Prof. Komiyama on the study of conformational change of protein cytochrome b-562 absorbed on colloidal gold particles. Cytochrome b-562 is a small cylindrical haem protein (diameter ~2.5 nm and height ~5 nm) found in the periplasm of *E-coli*. Depending on the degree of coverage, the protein on the gold particles (diameter ~ 31 nm) can be in side-on or tail-on conformation. Maximum optical shift occurs when protein particles are in side-on conformation with an effective composite particle size of 36 nm. Other work in this area includes the synthesis of semiconductor/semiconductor (such as CdS/PbS) and metal-coated (such as AuS/Au, Ag/polydiacetylene) particles. Some of this work was partially inspired by the theoretical work carried out while Prof. Haus was visiting Tokyo University on leave from RPI in 1992. In recent years, special emphasis has been placed on experimental projects because of the great influx of equipment funds from the government. At present, nanoparticles are fabricated by colloidal chemical vapor deposition and physical vapor deposition techniques (e.g., laser ablation, sputtering, and electron cyclotron resonance).

Dr. Fumihiro Wakai was invited by Prof. Komiyama to make a presentation on his work on superplasticity. Dr. Wakai was associated with the National Industrial Research Institute of Nagoya. He is now a professor at the Center of Materials Design at the Tokyo Institute of Technology in Yokohama. His work (*Nature* 1990. 344:421) on Si_3N_4/SiC composites has led to the discovery of superplasticity in nanocrystalline covalent ceramic materials. Currently, he is also the director of a large cooperative project between Japan and Germany (Prof. Fritz Aldinger, Max-Planck-Institut für Metallforschung), supported by the Japan Science and Technology Corporation, that commenced its operation in October 1966. The objectives of the cooperative project are to explore the nanostructures of the superplastic grain boundaries and to develop new synthesis techniques for maximum superplastic deformation at elevated temperatures. In addition, Prof. Komiyama mentioned the possibility of investigating the miniaturization of superplastic testing and characterization with a very small amount of materials.

CONCLUDING REMARKS

Although I spent all of my visit with Prof. Komiyama’s group, there are several other groups at the University of Tokyo that are conducting significant research in nanotechnology. These include the Physics Department (theoretical and experimental work on quantum-confinement and functional materials) and the Department of Applied Chemistry (TiO_2 particles).

Although my two-hour visit concentrated on composite nanoparticles/nanostructures as described above, I know from my previous visit in October 1996 that Prof. Komiyama is also active in areas related to amorphous silicon and other metal and semiconductor nanostructured materials. He is one of the research leaders in the one-step CVD synthesis of AlN, TiN, SiN, SiC, TiC, and ZrO (single or two components) nanostructured materials.

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Date Visited: 24 July 1997

WTEC: H. Goronkin (report author), E. Hu, L. Jelinski, M.C. Roco, D. Shaw, C. Uyehara

Hosts: Mr. Haruo Nakatsuka, R&D Center
Dr. Koichiro Inomata, R&D Center
Dr. Masaaki Tamatani, Materials and Devices Research Labs
Dr. Shuji Hayase, Materials and Devices Research Labs
Dr. Takashi Kawakubo, Materials and Devices Research Labs
Dr. Atsushi Kurobe, Advanced Research Laboratory
Mr. Kunio Yoshihara, Advanced Semiconductor Devices Research Laboratories

BACKGROUND

Toshiba has a history over 100 years. In 1939, Shibaura Engineering Works and Tokyo Electric Company were merged to a single company named Tokyo Shibaura Electric Company. In 1978, it changed its named to Toshiba Corporation.

Toshiba has a 3-layered R&D organization with long-, medium- and short-term elements: the corporate laboratories work on new technology that may be applied to products 5 to 10 years later; the development laboratories are working on technology for deployment 3 to 5 years later; the engineering departments in the operating divisions have as their most important task the solution of problems inherent to present products.

RESEARCH AND TECHNICAL HIGHLIGHTS

The following sections summarize the ongoing work in various Toshiba laboratories concerned with nanostructure technologies, based on presentations made to the WTEC panel by our hosts.

A. Kurobe, Advanced Research Laboratory

"Study of Shapes Produced by Stranski-Krastanov Growth in Cold-Walled UHV-CVD"

With a silicon buffer, hut-shaped Ge dots with (001 x 010) alignment were obtained. Without a buffer, dome-shaped Ge dots were obtained. Using H-terminated Si wafers by exposure of atomic hydrogen, domes were obtained.

The H-free wafers with a prior annealing at 750^{o}C contained the hut dots. Thermal desorption spectroscopy supports the difference in the surface: Dihydride desorbs at 415^{o}C. Monohydride desorbs at 550^{o}C. Annealing at 750^{o}C removes all H. Atomic hydrogen exposure produces a monohydride surface. The goal is study of interaction of dots with 2DEG. The plan is to move to a SiO_2-Si system to increase barrier height.

K. Inomata, Research and Development Center

"Advanced GMR"

Working on spin electronics for high density heads, 20 Gbit in 2002 is forecast. Toshiba researchers have achieved >10% GMR ratio in layered films at room temperature. They have also achieved > 30% in nanogranular films with a coercive field of 0.1 T.

The most promising approach is the tunnel junction. It has > 25% MR ratio but drawbacks include high resistance and strong fall-off of the magnetoresistance ratio with applied voltage and pinholes in the ultrathin insulator barrier.

Dr. Inomata described two structures for possible use in future memory and logic. One new proposed structure consists of two ferromagnetic (FM) layers sandwiching a barrier containing 8 nm granules of FM material in an SiO_2 matrix. The total barrier thickness is about 10 nm. Inomata and coworkers explained that the size and distribution of the FM granules must be carefully controlled. The FM contact polarization can be switched either parallel or antiparallel to the granules and to each other to provide high or low current transport through the barrier. No data were provided.

A second proposed structure places the two FM electrodes on the same surface of granular FM materials. This is a transistor structure in which lateral conduction can be controlled by the relative polarization of the contacts. No data were provided.

T. Kawakubo, Materials and Devices Research Laboratories

"Epitaxy of Ferroelectric (FE) Materials"

The goal of this project is to control FE properties by orientation and strain of the epitaxial material.

The researchers use (Sr, Ba)TiO_3 with $SrRuO_3$ electrodes, which have good metallic conduction. By reducing the thickness and sputter conditions, good performance (saturating hysteresis loop) at 1.0 V has been obtained. This material is also under investigation for DRAM charge storage capacitors. With 20% Ba content, the dielectric constant is about 900. An SiO_2 equivalent thickness of 0.085 nm was obtained. The leakage current was 4×10^{-8} A/cm^2 between ±1.3 V. This was said to be satisfactory for 0.12 μm DRAM. TiAlN/Pt barrier layers were used.

M. Tamatani, Materials and Devices Research Laboratories

"Nanoparticle Phosphors Made by Thermal Plasma"

This project produces spherical particles compared to faceted particles. These particles have the particle size in the same region as those of commercially available materials. They must be heat treated in oxygen or hydrogen to restore luminescence efficiency comparable to that of the commercial phosphors. The thermal plasma also produces nanoparticle phosphors, which could be used as labeling agents for analysis.

Site: **ULVAC Japan, Ltd.**
Vacuum Metallurgical Company (VMC)
516 Yokota, Sanbu-cho, Sanbu-gun
Chiba 289-12, Japan
Fax: (81) 467-87 3383

Date Visited: 23 July 1997

WTEC: D. Shaw (report author), C. Koch, R.W. Siegel, C. Uyehara

Hosts: Dr. Chikara Hayashi
Dr. Masaaki Oda

BACKGROUND

The Vacuum Metallurgical Company (VMC) is a subsidiary of ULVAC Japan, Ltd., which is a relatively large conglomerate of 30 companies employing over 3,500 people. The principal products of VMC include sputtering targets; complex shaped Ti-alloy cast parts; reactive and refractory metal sheet, wire, and shapes; and service coating for processing equipment for semiconductors, display panels, etc.

VMC's ultrafine-particle (UFP) business is based on early work by Dr. Hayashi and colleagues on gas-phase particle nucleation (evaporation and condensation) and deposition by using nanoparticles dispersed in tiny gas jets (in the 10 micron diameter range). VMC commercialized magnetic UFP in 1971, and Dr. Hayashi (at the time, president of ULVAC) served as the leader of a UFP project in Japan's Exploratory Research in Advanced Technology (ERATO) program from 1981-1986. ERATO has been supported by the now renamed government organization, Japan Science and Technology Corporation (JST). The UFP project investigated the physical, chemical, and biological properties of nanoparticles.

Over the years, VMC has improved the magnetic UFP technique and now offers a large quantity of metallic and organic particles; gas-evaporation and gas-deposition equipment for producing fine pattern of contacts and conductive lines for electronic devices; and UFP paste (dispersed liquid) with coating system.

RESEARCH AND DEVELOPMENT HIGHLIGHTS

Although the basic design of the induction-heating chamber for the ultrafine-particle generation was developed by Hayashi and Oda in the

1970s, the performance of the chamber has been steadily improved through a series of government-subsidized R&D programs at VMC. At present, there is an impressive list of UFPs that are produced in large scales under reasonably controlled conditions. These include chain-aggregate ferromagnetic UFPs, metallic (e.g., Au, Ag, Cu, Pd, Ni, Al, Sn, etc.) isolated UFPs, and coated UFPs (e.g., ZnO-coated Cu and polymer-coated Fe). These particles are used for the formation of thick films for various applications, including electronics, optics, etc. Application fields presently being pursued by VMC are shown in Table D.1.

CONCLUDING REMARKS

VMC is in many ways similar to Nanophase Technologies Corporation in the United States. They both use the principle of gas-phase condensation for particle generation. Both are market-driven companies that try to break into various new markets. Thus, their targeted markets, as shown in Table D.1, are very similar. At the present time, the UFP revenue for VMC is about $4 million. Dr. Hayashi indicated that he hopes to increase the UFP business in VMC to about $10 million in two or three years.

TABLE D.1. UFP Applications and Processes at VMC

Applications	Coating Methods	Effects
ELECTRONICS		
Metalizing of ceramic parts (Eliminating electric discharge)	Dipping or printing	Reduce processes and materials (replacing vacuum deposition)
Formation of electrodes of chip condensers	Dipping	
Formation of test circuits	Drawing with a microdispenser	Decrease firing temperature
Repairing of electric circuit of LCDs or PDPs	Repainting with a microdispenser	
Formation of electric circuits	Screen printing	
OPTICS		
Coating of infrared reflectors	Dipping	Reduce processes
Coating of laser reflectors		
Repairing of reflectors		
ARTS		
Decoration of ceramics or glass utensils	Pad painting	Reduce processes, decrease firing temperature
Coating of accessories	Dipping	Replace electroplating
Replacing of gold leaf	Spraying	Reduce processes

NOTES ON FUNDING OF NANOTECHNOLOGY RESEARCH IN JAPAN

M.C. Roco

Introduction

Government organizations and very large corporations are the main source of funding for nanotechnology research and development in Japan. Small and medium-size companies play a minor role. All large Japanese corporations devote a significant portion (generally ~ 10% in the electronics industry) of their income to R&D. Japanese corporate research tends to be product-oriented, but there is also a well-established culture within the corporate and scientific community of planning for the next generation of technological innovation. As evident in the foregoing site reports, nanotechnology R&D is decidedly a part of the present and future planning of both government and industry labs, and funds are allocated accordingly.

Government funding for nanotechnology research should be viewed in the context of the overall increase of public support for basic research since 1995 as a result of passage of Japan's Science and Technology Basic Law No. 130 (effective November 15, 1995). The law proposes to allocate approximately ¥17 trillion (~$148 billion[1]) for basic research to Japanese universities, industry, and national laboratories from 1996 to 2000. The main recipients of the 1996 government budget for science and technology ($23.3 billion/year) were the Ministry of Education, Science, Sports, and Culture (known as Monbusho), which received 46.5% of the S&T budget; the Science and Technology Agency (STA), which received 25.9%; and the Ministry of International Trade and Industry (MITI), which received 11.9%. In 1997 the university system received $935 million from Monbusho as "grants-in-aid" for research, and $239 million from other ministries, however, it appears that the ministry with the largest allocation of funds specifically earmarked for nanotechnology R&D is MITI.

The information on funding presented here is based on interviews with Japanese colleagues during the WTEC panel's visit in July 1997, using the nanotechnology definition adopted by this study. All budgets are for the fiscal year 1996 (April 1, 1996 to March 31, 1997) and are approximate. In many institutions it was difficult to separate the exact contribution of research related to nanostructure science and technology, and for those institutions, only the total budget, as available, is given.

[1] The exchange rate used throughout this overview is ¥115 = $1, unless otherwise stated; the budgets given are for FY 1996.

A. Main Japanese Government Organizations Sponsoring Nanotechnology R&D

MITI / AIST (Agency of Industrial Science and Technology)

Total budget, $2.75 billion/year; nanotechnology budget from all sources below, ~$60 million/year

National Institute for Advancement of Interdisciplinary Research (NAIR), Tsukuba City

- Joint Research Center for Atom Technology (JRCAT), ten-year budget of ~$220 million (1992-2001); $25 million/year
- Research on Cluster Science, ~$10 million (1992-1997); $2 million/year
- Research on Bionic Design, ~$10 million (1992-1997), 50% for nanotechnology; $1 million/year

Electrotechnical Laboratory, Tsukuba City

- Total budget, ~$100 million/year; nanotechnology budget, ~$17 million

Osaka National Research Institute, Osaka

- Total budget, ~$26 million/year; estimated nanotechnology budget, ~$3 million/year

National Industrial Research Institute of Nagoya (NIRIN), Nagoya

- Total budget, ~$25.2 million/year (1996); estimated nanotechnology budget, ~$2.5 million/year

MITI's Quantum Functional Devices (QFD) Program

- Ten-year budget ~$64 million (1991-2001); estimated nanotechnology budget, ~$6.4 million/year

Science and Technology Agency (STA)

Total budget, $6 billion/year; estimated nanotechnology portion was ~ $35 million/year in FY 1996

Institute of Physical and Chemical Research (RIKEN), Wako City

- Total budget, $300 million/year; nanotechnology budget is included in Frontier Materials research

National Research Institute for Metals (NRIM), Tsukuba City

- Total budget, $130 million/year; nanotechnology work in various projects

National Institute for Research in Inorganic Materials (NIRIM), Tsukuba City

- Total budget, $35 million/year; nanotechnology budget, ~$0.8 million

Japan Science and Technology Corporation (JST)

- Administration of ERATO Program (Exploratory Research for Advanced Technology), including 4 nanotechnology projects, each with total budgets of $13-18 million for five years:
  - Quantum Wave Project (1988-1993)
  - Atomcraft Project (1989-1994)
  - Electron Wavefront Project (1989-1994)
  - Quantum Fluctuation Project (1993-1998)

Ministry of Science, Education, Sports, and Culture (Monbusho)

Total budget, $10.8 billion/year

Nanotechnology programs are supported at universities and national institutes, as well as via the Japan Society for Promotion of Science (total resource allocation unknown).

Tokyo University, Tokyo

- University of Tokyo's Research Center for Advanced Science and Technology
- Institute of Industrial Engineering
- Chemical Engineering (H. Komiyama) (A newsletter "Quantech" for a loose network on nanotechnology in Japan is edited here)

Kyoto University, Kyoto (H. Shingu)

Tokyo Institute of Technology, Yokohama (M. Aizawa)

- Bioelectronic Devices—10 year MITI project was completed in 1996

Tohoku University, Institute of Materials Science, Sendai

- Total budget, $44 million/year

Nagoya University, Nagoya

Osaka University, Osaka, K. Niihara's lab

- Total budget, $25 million/year

Institute of Molecular Science, Okazaki (M. Fujita)

Exploratory Research on Novel Artificial Materials and Substances for Next Generation Industries

- Five-year university-industry research project sponsored by the Japan Society for the Promotion of Science (JSPS), part of Monbusho "Research for the Future" Program

– e.g., at IMR, Tohoku University, JSPS funds "Nanostructurally Controlled Spin Depending Quantum Effects and New Electronics and Magnetics"; total 5-year budget 1996-2001, $3.8 million

B. Industry

Hitachi Central R&D Lab., Tokyo (T. Ikeda)

Annual sales Hitachi are about $70 billion/year; R&D spending as percent of total sales is on the order of 10%. There are seven corporate laboratories with 3,000 personnel. Nanotechnology takes a significant percentage of precompetitive research at Hitachi, perhaps as much as $280 million per year.

NEC Fundamental Research Laboratories, Tsukuba (J. Sone)

Annual sales are about $40 billion/year; R&D is 10% of total sales; Precompetitive research (Central group) spends about 1% (or $30 million per year); Nanotechnology-related precompetitive research is 50% of that (or $15 million/year); it also receives partial support from government (for example, 20% of funding for devices)

Toshiba Research Center

Annual sales are $52 billion/year; R&D expenditures as a percentage of total sales are comparable to other Japanese corporations; nanotechnology-related precompetitive research is about $20 million/year.

Nihon Shinku Gijutsu (ULVAC)

Vacuum Metallurgical Co., part of a conglomerate of 35 companies, had at the time of the WTEC visit ~$4 million in particles sales per year for electronics, optics, and arts; it planned to expand that investment to ~ $10 million/year within three years. A major focus of ULVAC is marketing.

Other companies with large nanotechnology research programs are NTT, Fujitsu, Sony, and Fuji Photo Film Co.

Comments

Strengthening of Japan's nanotechnology research infrastructure in the past several years has been fueled by both the overall increase of government funding for basic research and by larger numbers of academic and industry researchers choosing nanostructured science/technology as their primary field of research. The main drivers are technological innovation and potential industrial applications, with several exceptions where the driver is scientific curiosity. A system approach has been adopted in most laboratory projects, including multiple characterization methods and processing techniques for the same objective. The university-industry interaction is stimulated by new MITI projects awarded to universities in recent years that encourage use of research personnel from industry. Issues that are being addressed already are more extensive use of peer review, promotion of personnel mobility and intellectual independence, rewarding researchers for patents, promotion of interdisciplinary and international interactions, and better use of the physical infrastructure. The three major government organizations (MITI, STA, and Monbusho) allocated an estimated total of $120 million for nanotechnology in fiscal year 1996.